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OIL SLICK DISPERSAL MECHANICS

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16. ABSTRACT

This study investigates the spreading and dissolution behavior of small oil slicks formed from spills of 12 oils. The increases in area covered by the oils during spreading experiments were determined using photographic techniques. Spreading equations were derived and used to correlate experimental data. Derivation of the equations parallels Fay's development.

The rate of dissolution of the oils in tap water at 25°C were investigated by equilibrating oils with water in open static tests. Limits of solubilities have been established for the oils from results of long-term equilibration in closed vessels. Six oils were also equilibrated with salt water. A segmented mathematical model has been derived and used to correlate experimental data. The model describes two processes that occur during equilibration: soluble and volatile components of oil leach into solution initially, and later evaporate from solution.

Finally, a detailed description of the mass transfer process occurring during chemical dispersion of oil spills has been made. The primary mechanisms have been quantified by analogy to homogeneous and heterogeneous catalysis and detergency. To evaluate the effectiveness of five commercial dispersants, a large-scale laboratory system has been designed. Parameters investigated include oil and dispersant types, oil-to-dispersant ratios, degree of agitation, and the effect of salt water.

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FOREWORD

The U. S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Crude oils and petroleum-based products are extremely complex systems and behave differently when discharged to marine environments. This study investigates the spreading and dissolution behavior of small oil slicks on water. The use of chemical surface-active agents to disperse oil slicks was also evaluated in experiments conducted under controlled conditions in the laboratory.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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PREFACE

During the past five decades, petroleum has become the world's major source of fuel and power. As a consequence of the rapidly increasing demand for petroleum, the volume of crude oils and refined products handled during the production, transportation, and chemical manufacturing processes has increased dramatically. Anderson (1967) estimates that oil accounts for a third of world shipping tonnage.

This dependence on oil is causing increasing oil pollution of marine environments by accidental discharges from tankers and oil-ferrying vessels, from rupturing off-shore oil-wells, and as a result of natural seepage. Intentional discharges of bilge and ballast water further aggravate oil pollution. Several key sources of oily discharges into the marine environment were identified in a report by the National Academy of Sciences (1975). This report estimates the annual influx of oil into the oceans at 6×10^6 metric tons. A major fraction of the influx was attributed to spillage during tanker collisions, natural seepage, and oil well mishaps.

Oil pollution of marine environments has been occurring during the past decades, but public awareness of the problem did not intensify until the Torrey Canyon Spill in 1967 and the 1969 oil well blow-out in Santa Barbara Channel. Before these incidents, autodepuration processes were considered adequate cleansing mechanisms for oil pollution of all natural water bodies. The increasing size of oil-transporting vessels with reduced manueverability and the shift of oil prospecting to shallow waters of the outer continental shelf have caused considerable concern. News media coverage of oil spills from recent tanker collisions has maintained public interest. Pictures of dead oil-soaked fowl and fish and tarry oil lumps that wash ashore to deface clean beaches make emotional issues.

Because of the many problems caused by oil spills and concern for a clean marine environment by the public and environmentalist groups, legislation has been enacted at both national and international levels to curb oil pollution. During recent years, research in oil pollution has increased as many laboratories try to provide answers to numerous questions concerning the inputs, fates, and effects of petroleum in the marine environment.

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Initially, research studies focused on developing adequate equipment and devices for containment, removal, and clean-up of spilled oil. Oil spill clean-up is a difficult problem for several reasons:

a) Oil spills occur at random, and the portion of the earth susceptible to oil spills is large: Approximately 70% of the earth is covered with water and 60% of world oil production is transported across the oceans;

b) A majority of the world's coastlines are scattered and inaccessible in the event of an oil spill;

c) In the presence of the enormous forces generated by winds, waves, and currents, oil slicks can cover large areas of the ocean surface in a short time; thus the logistics of dealing with large oil spills in remote areas can be overwhelming.

More recent research efforts have been focused on ecological studies to understand the short- and long-term biological effects of oil pollution on marine organisms. Success in these two research areas has been limited because of lack of understanding of the physics and chemistry underlying the dispersal processes that act on oil after a spill occurs. Research into the physical, chemical, and mechanical processes that disperse the components of crude oils is necessary, and the rate of each process has to be quantified. Knowledge of these rates will be useful for evaluating the biological effects of petroleum on marine biota and future decisions on development of more effective clean-up methods.

Since coastal waters are the most productive part of the sea, containment and physical removal of oil slicks are the favored methods for oil spill clean-up. Present technology in booms and skimming devices limits their use to calm waters. Thus in consideration of potential ecological damage to fish populations and coastal marshes, as well as fire hazards from large oil spills, use of chemical oil dispersants appears to be a promising option, especially in view of the nontoxic nature of the new generation of dispersants. The number of commercially available dispersants is large, however, and manufacturer's claims for these dispersants are difficult to evaluate and/or substantiate. In the absence of detailed laboratory studies, a realistic approach to dispersant application cannot be developed. The role of dispersants and the mechanistic steps in the breakup and reformation of oil slicks following dispersant application are poorly understood.

Recognition of these information gaps has provided the stimulus for this research study on oil slick dispersal mechanics,

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particularly in the areas of spreading, dissolution, and chemical dispersion.

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ABSTRACT

This study investigates the spreading behavior of small oil slicks formed from spills of 12 oils. The oils included crudes of different origins as well as processed oils. The increases in area covered by the oils over time were determined using photographic techniques. Spreading equations were used to correlate experimental data. These equations contain the physical properties of oil and water phases, volume of oil spilled, and time of spreading as independent variables. Derivation of the equations parallels Fay's development. Results show that gravity, surface tension, and viscous forces are important in spreading. Oil slick configurations vary for different oils, and profiles are neither rectangular, circular nor spherical.

The rates of dissolution of these oils in tap water at 25C were investigated by equilibrating oil with water in open static systems for 2 to 3 weeks. Limits of solubilities have been established for the oils. Six oils were also equilibrated in salt water at 25C. The concentration-time profiles of the oils vary in tap and salt water tests. Concentrations of oil in solution are lower in tests with salt water. A segmented mathematical model has been derived and was used to correlate experimental data. The model describes two processes that occur when oils are equilibrated with water: soluble and volatile components of oil leach into solution initially and later evaporate from solution. Experimental data confirm the nonequilibrium nature of dissolution and evaporation processes. The concentration of oil in the water column may be toxic to marine organisms at certain times during equilibration processes.

A large-scale laboratory system has been designed and was used to evaluate the efficiencies of five commercial dispersants. Parameters investigated include oil-to-dispersant ratios, oil type, degree of agitation, and the effect of salt water. The mass transfer processes which cause chemically treated slicks to break up into oil droplets and to disperse into the aqueous phase upon agitation, have been identified. The primary mechanisms have been quantified by analogy to homogeneous and heterogeneous catalysis and detergency. Phenomenological theories have been developed for chemical dispersant action at the oil/water interface and in the near-field water column. The use of chemicals to disperse oil slicks must be viewed as a

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management alternative based on knowledge of the toxicity of dispersants to aquatic biota and interactions with oil/water systems.

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ABBREVIATIONS AND SYMBOLS

a	constant or acceleration of the oil, cm/sec^2
A	surface area, interfacial area, or volume of oil per unit length normal to the direction of spreading, cm^2
b	constant or width of the oil slick, cm
c	constant
C	concentration, mol/cm^3 or mg/ℓ or gm/cm^3
ΔC	concentration difference, mol/cm^3
$\overline{C}$	average concentration, mg/ℓ
C*	interfacial concentration of oil, mg/ℓ
(C_iS)	interfacial concentration of adsorbed dispersant molecules, mg/ℓ
(C_mO)	interfacial concentration of mixed micelles, mg/ℓ
(C_mOS_m)	interfacial concentration of adsorbed mixed micelles, mg/ℓ
C_p	solubility in water of pure hydrocarbon, mol/cm^3
C_w	concentration of hydrocarbon in bulk water phase, mol/cm^3
d	diameter of oil droplet, cm, or distance between charged micelles, cm
D	diffusion coefficient, cm/sec
$\overline{D}$	average diffusion coefficient, cm/sec
e	solubility enhancement factor
E	energy of adsorption or desorption, cal/gm-mol
f	dilution factor
F	flux of compounds through unit area, mg/cm^2·day, or force per unit volume of oil, dynes/cm^3
Fo	spreading force due to net surface-tension of oil, dynes/cm
Fm	external spreading force by a control monolayer, dynes/cm

g	acceleration due to gravity, cm/sec^2
h	thickness of oil layer, cm
Δh	thickness of oil layer above water level, cm
H	wave height, cm
k_i	constants, or reaction/diffusion coefficients, time^{-1} (i = -3,-2,-1,1,2,...)
k_o	frequency factor, time^{-1}
K	diffusion coefficient, time^{-1}
$K_{1,2,3}$	equilibrium reaction constants
K_r	Blokker constant
ℓ	length of a slick, or characteristic length of a slick in the direction of spreading, or wave length, cm
L	wave length, cm
m	number of carbon atoms or adsorption sites, or aggregation number of dispersant molecules
n	number of molecules per unit cross sectional area, molecules/cm^2
N	flux of compound, mol/cm^2·sec
N_A	Avogadro's Number, 6×10^{23} molecules/gm-mol
N_B	Boltzmann's constant, dynes·cm/K
O	interfacial concentration of oil, mg/ℓ
p	number of counter-ions not attached to the micelle
P	rate of permeation, mg/cm^2·sec, or hydrostatic pressure, gm/cm·sec^2
ΔP	hydrostatic pressure difference, gm/cm·sec^2
q	volumetric flow rate, cm^3/sec
Q	volumetric flow rate, cm^3/sec
r	radius of oil slick, micelle or single dispersant molecule, cm
$r_{1,2,3}$	rate of reaction for steps 1, 2 and 3, mg/ℓ·sec
$r_{A,D,R}$	rate of reaction for adsorption, desorption, and reaction controlling steps
R	gas constant, cal/gm-mol. K, or combined rate of accommodation/solubilization/microemulsification, mg/ℓ·sec
$R(t)$	radius of oil slick as a function of time of spreading, cm

S	solubility of oil in water, mg/ℓ, or adsorption site
S_o	total concentration of adsorption sites
t	time, sec or day
t_D	duration of spill, sec
t_m	time to attainment of maximum concentration, day
t_s	Saybolt universal seconds, sec
T	absolute temperature, K
u	velocity of flowing water, cm/sec
v	velocity, cm/sec or ft/sec or knots
$\dot{v}$	volumetric flow rate of oil, cm^3/sec
V	volume, cm^3
V_r	rise velocity of an oil droplet, cm/sec
V_s	volume of a water sample
w	width of an oil slick, cm or van-der-Waals adsorption energy associated with $-CH_2-$ group, cal/gm-mol
W	mechanical energy or work input, ergs
x	distance in the horizontal direction, or coordinate of the center mass of the oil slick, cm
X	mole fraction of compound
y	distance in the vertical direction, cm
z	distance normal to the plane across which mass transport occurs, cm
z_1	valency of surface-active ion

Greek Symbols

σ	surface-tension, dynes/cm
ρ	density,gm/cm^3
$\Delta\rho$	ratio of oil and water densities
ν	kinematic viscosity, cm^2/sec
δ	thickness of interfacial layer, cm
δx	unit length along the direction of spreading of oil slick, cm
ε	electron charge, or energy input per unit mass and time, ergs/gm·sec
ψ_o	electrical potential of the surface
γ	activity coefficient

Γ	modified concentration, mg/cm^2
θ	fraction of the surface which is unoccupied by adsorbed molecules
$\theta_{1,2}$	instantaneous contact angles formed by the oil phase at the air and water boundaries, degrees
ϕ	weight fraction of the total volume of solution occupied by micelles
μ	absolute viscosity, gm/cm·sec
λ	ratio of width to length of slick

Subscripts

b	boundary
c	current, counter-ions or calibration
crit	critical
d	diffusion or dispersant
E	evaporation
eq	equilibrium
f	forward
g	gas phase
H	refers to Henry's Law
i	ionic, single molecule or specie
L	liquid phase
m	aggregation number of micelles or maximum
n	non-ionic or nth compartment
o	oil
ow	between oil and water
p	polarization
r	reverse
s	saturation
t	total
w	water phase, wave or wind
x	horizontal direction
y	vertical direction
0	zero
95	95 percent
∞	equilibrium, bulk of air or when time is equal to infinity

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SECTION 1

INTRODUCTION

After an oil spill occurs, several natural processes begin to operate on the oil and cause it to disperse. The physical, chemical, and mechanical processes that disperse components of crude oils have been identified (Pilpel, 1968; National Academy of Sciences, 1975; McAuliffe, 1977a), but the rates of the individual processes remain to be quantified. In the early stages of an oil spill, the major dispersal mechanisms are natural spreading, evaporation, emulsification, dissolution, and mechanical transport by winds, waves, and current forces. During the latter stages of an oil spill, other processes (e.g. microbial decomposition, oxidation [atmospheric, chemical, and photo-], adsorption onto particulate matter, sedimentation, etc.) continue to dissipate the oil. These processes do not act singly but compete with each other, and the complex nature of the interactions often makes it impossible to separate and quantify individual rates. Figure 1 shows the processes involved in the fate of oil in the marine environment.

The action of a specific dispersal process on oil components and the effect on environmental damage caused by the oil spill depends on a combination of factors. Straughan (1972) has discussed some of the factors: the type of oil, the dosage rate of oil, the physiography at the site of the spill, weather conditions at the time of the spill, the biota of the area, the season of the spill, previous exposures of the area to oil and other pollutants, and the method used to treat the oil.

To predict the fate of oil spilled in a marine environment, it is necessary to quantify the rates of the different dispersal mechanisms. Knowledge of how fast crude oils and petroleum products spread on calm water and in the presence of external forces (winds, waves and currents) is essential before management decisions can be made to contain the oil by booming and/or to initiate skimming operations. Information on the rates of dissolution and characteristics of emulsification of specific oils is useful for assessing hydrocarbon concentration levels in water to which marine organisms will be exposed. Until these processes are understood fully speculation will continue on the short- and long-term effects of oil pollution on marine environments.

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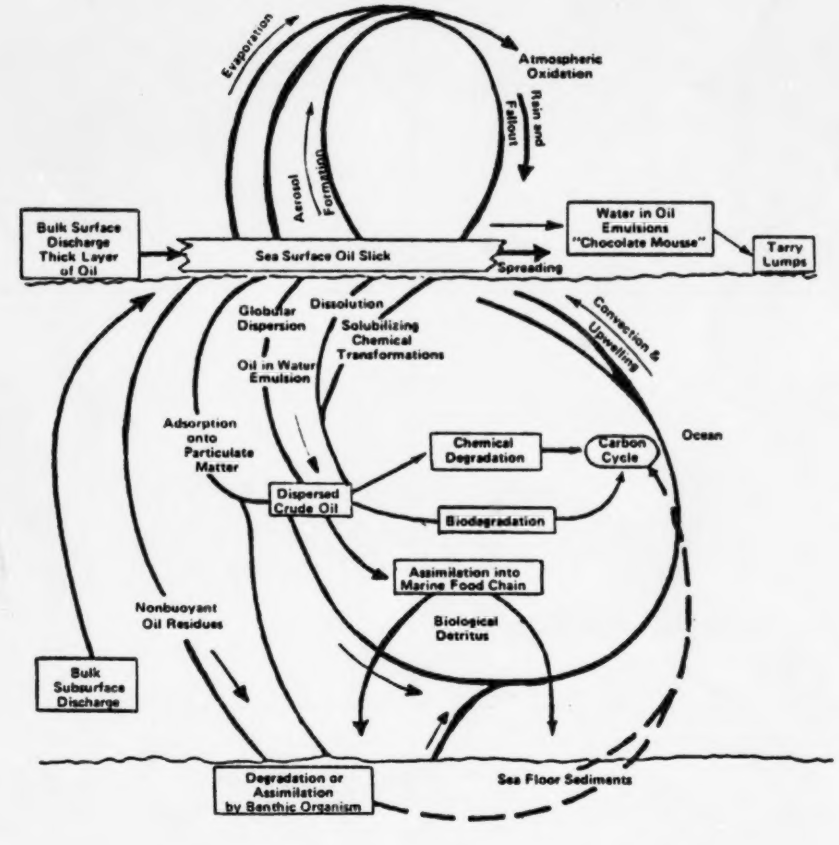

Figure 1. Processes Involved in the Fate of Spilled Crude Oil in the Marine Environment (Burwood and Speers, 1974)

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Because the limitations of oil containment and skimming devices in rough water are becoming evident, other options to deal with oil spills must be considered. The addition of chemical dispersants to oil slicks to stimulate the formation of oil droplets and enhance their dispersal into the underlying water now appears to be an acceptable clean-up option in view of the irreparable damage to coastlines and marine life that can result from large oil spills. Dispersants are easy to use. In remote areas, adequate mixing between oil slicks and dispersants can be obtained from the turbulence generated by wind, wave and current forces at sea without additional mixing energy. The mechanisms of dispersant action on oil slicks have not been investigated, and a rational approach to dispersant application has not evolved.

The number of crude oils and petroleum products that can be spilled on water is large. The behavior of oils on water even under similar spill conditions will vary due to different chemical compositions. Thus, there is a need for research studies with several oils in order to quantify (if possible), or to determine the order-of-magnitude estimates of the rates of dispersal processes for specific oils. Appropriate plans for contigencies to mitigate the damage to marine environments can be made more accurately when the rates and mechanisms of oil transport are known.

SECTION 2

CONCLUSIONS

Oily discharges to aquatic systems are usually marked by slick formation. Surface oil layers that form after spills have many undesirable impacts on the environment, such as aesthetic damage to beaches and shoreline, reduction of oxygen exchange at the air-water interface, fouling of wild fowl, etc. The potential for damage by oil spills depends on the rates of the dispersal mechanisms and other factors. Spreading and dissolution of oils in the underlying water are important dispersal mechanisms, but these rates have not been quantified for many petroleum-based systems.

Crude and processed oils are extremely complex systems and behave differently when discharged to the environment; the origin and composition of oil, processing history, and physical and chemical properties determine the rates of spreading, dissolution and other dispersal mechanisms. In this study, the rates of dissolution and spreading of 12 oils were investigated under laboratory conditions.

Rates of spreading were determined experimentally by measuring the extent of areal covering with time of small oil spills on calm water. Four different volumes of oils were spilled and the areas covered by the slicks were determined photographically. As the oils have different physical and chemical properties, the variables investigated include, density, viscosity, surface tension and interfacial tension between oil and water. Observations of the configurations of the spreading slicks indicated that the oils did not spread preferentially as rectangular, circular or elliptical slicks. In general, the shape of a slick varies according to the type of oil spilled, the rate of discharge and other factors. It is influenced by thermal convection currents and molecular motions in the water column.

Mathematical models were derived for oils spreading on calm water. The derivation of the spreading equations follows Fay's work. The principal forces influencing spreading of oils on calm water are gravitational, viscous, inertial, and net surface tension. Gravity accelerates spreading, causing oil slick thickness to decrease and the oil to spread laterally. Viscous and

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inertial forces retard spreading, but the effect of the latter appears to be small. The value of net surface tension determines whether spreading is accelerated or retarded. These forces are related to the physical properties of the oil and water phases.

By equating an accelerating force to a retarding force, several spreading models containing only one empirical constant can be derived (Fay, 1971). The models fit the experimental data with varying accuracies. In general, the order of goodness of fit, from best to worst, was gravity/viscous, surface-tension/viscous, gravity/inertia and surface-tension/inertia. The surface-tension/inertia spreading model is independent of the volume spilled; this equation is not valid for predicting the aerial extent of slicks. The effects of physical properties of the oil and water phases can be determined from the spreading equations. The effect of temperature on rate of spreading was not investigated, but it can be determined from indirect influence on the physical and chemical properties of the oil and water phases.

In the open sea, calm conditions do not persist indefinitely. Gross oil transport by natural turbulence is superimposed on spreading and the total area covered by a slick must be determined by summing the transport by the two mechanisms.

The rates of dissolution of the oils were determined by measuring their solubilities in water during equilibration in open static tests. The oils were equilibrated with tap water at 25C for 2 to 3 weeks. Experimental data show increases in oil concentrations initially and decreases later during the period of equilibration. Similar trends were exhibited by the experimental data generated by equilibrating 6 oils with salt water solution, however, solubilities were lower in tests with salt water, and the oils attained maximum solubilities at slower rates. Saturation data were determined from long-term, closed-system experiments. Solubilities vary for different oils and depend on oil composition. Organic species in solution were not characterized, but they are believed to be low molecular weight hydrocarbon compounds, for example aliphatics, aromatics, and substituted organics.

The experimental data suggest that as oil slicks equilibrate with water, volatile hydrocarbon species evaporate into the atmosphere from the air/oil interface, and soluble species dissolve into the underlying column of water from the oil/water interface. These processes are not in equilibrium; hydrocarbons continue to evaporate from solution after the oil layer has been depleted of volatile hydrocarbons. This process occurs even when oil is present in solution at less than saturation concentrations. A segmented mathematical model was proposed to quantify the rates of dissolution for the duration of the equilibration period. This model consists of equations for the solution and evaporation phases. The model was used to fit experimental data from the dissolution studies. The results of the numerical simulation show that the model fits experimental data for a majority of the oils fairly well.

The conditions during the dissolution experiments correspond to an unlikely worst case of an oil spill such that the oil completely covers the water surface. Under these conditions, experimental data suggest that low concentrations of oil will persist in the water phase after 2 weeks of equilibration. In the field, the concentration of oil in the water column below surface slicks will be influenced by several factors, such as water quality. For example, dissolved organic matter is present at varying concentrations in aquatic systems. Dissolved organic matter can solubilize organic compounds and increase oil concentration. Water movements will have a dilution effect on concentration, but may cause oil droplets to be transported to the underlying column of water. Other processes which disperse and degrade petroleum operate simultaneously with dissolution. The concentration of oil in the aqueous phase will be influenced by the rates of these mechanisms.

Management decision to disperse oil spills with chemical dispersants must be based on knowledge of the action of commercial preparations and toxicity to marine organisms. This study has identified the mass transfer processes that lead to formation and dispersion of droplets in chemically-treated oil slicks. Mathematical equations are proposed to quantify the rates of some of the principal mechanisms. These equations were not verified with experimental data, since necessary input data includes information that is deemed proprietary or cannot be determined experimentally.

The efficiencies of 5 commercial products to disperse 3 oils of varying physical and chemical characteristics were evaluated in a large-scale laboratory system. The design of the wave-tank was based on current dispersion practices and the tank permits spatially distributed sampling. Variables investigated include oil-to-dispersant ratio, oil and dispersant types, and the effects of agitation and sea salts.

Experimental data show that efficiency increases with the volume of dispersants added. Oil concentrations decrease gradually with time after dispersion: the rate of decrease varied for each dispersant and oil combination. When the system is mixed continuously, agitation causes unstable and stable droplets to go initially into the aqueous phase. When agitation ceases, unstable droplets coalesce and migrate to the water surface, oil concentration in the aqueous phase decreases with time and, finally, stabilizes. The dispersants are classified according to the efficiency of their action under test conditions by measuring the quantity of extractable organic material in water samples.

This study investigated the rates of spreading, dissolution and chemical dispersion of petroleum: these processes are important mechanisms for the dispersal of oil spills. Previous research studies have identified the key processes and the relative importance of each process but research was limited to a few crude oils. Two crude oils from different sources may behave differently when spilled, even when their physical properties (density, viscosity, and surface tension) have similar values. Models for predicting the rates of spreading must be correlated with oil properties that can be measured easily using a representative sample of the oil slick. From the point of view of those charged with the responsibility of containing oil slicks, models based upon gross parameters (e.g. oil slick thickness) are of limited value due to the difficulty and error of measuring this parameter during the life of a slick. Calm conditions do not persist indefinitely in the field and ultimately, transport of gross oil by mechanical forces is superimposed on natural spreading.

The interactions of wind, waves, and tides in the presence of oil slicks cannot be adequately simulated in the laboratory. The mechanical transport of oil due to these forces is probably more important than natural spreading in the overall dispersion of oil slicks, when the damage to a coastline is considered. But the effects of these forces on oil slicks are known in general terms; oil slicks become elongated and distorted. Usually, the slick breaks into patches which drift in the direction of the wind at a speed proportional to the sum of the vector velocities created by transport forces. The influence of tides is minimal due to the periodic and oscillatory nature of tidal movements.

The dispersal of spilled oil by applying chemical dispersants appears to be a promising method of cleaning-up oil spills. Proper use of dispersants could result in the efficient dispersal of oil even in the absence of wave action. A gap in knowledge exists: the mechanism of action of dispersants must be better understood, and the rates of spreading and dissolution must be established for a larger variety of crude oils and petroleum products.

SECTION 3

RECOMMENDATIONS

Research on the rates of all oil dispersal mechanisms is needed to improve mass balance calculations. The variety of oils that can be spilled is large and marine ecosystems vary in susceptibility to the detrimental effects of spilled oils.

Research in the following areas is recommended:

1. Direct air sampling above slick surfaces to determine rates of evaporation of hydrocarbon species;

2. Rates of adsorption of oils on different sediments should be determined to characterize adsorption isotherms;

3. Decreases in rates of oxygen exchange across the air/sea interface, in the presence of different oils and film thicknesses;

4. Improvements in analytical determination of oil concentrations can be realized by coating sampling devices and glassware used for extraction, storage, etc., with hydrophilic films;

5. Experiments in coastal environments must be intensified to improve knowledge of the rates of physical oil dispersal processes and effects of oil on aquatic biota;

6. In the absence of information on the composition of commercial dispersants, analytical techniques must be developed to characterize water samples from dispersion studies in terms of only the hydrocarbon species contributed by oil slicks;

7. More critical comparisons of different dispersants for general detergent power are needed;

8. Further studies on the mechanisms of dispersant action are required, with emphasis on the effects of chemical structure of surfactants, solvent types, and other active components on dispersion efficiency;

9. Studies on toxicity of dispersants to marine life will increase knowledge on environmental impact aspects of dispersants;

10. Rates of penetration of oils and chemically-treated oils into sediments deserve to be investigated; and

11. Further development of the phenomenological theories of dispersant action is required.

SECTION 4

RESEARCH OBJECTIVES

Oil spills occur in the sea at random and without prior warning. A study of an actual spill in the field is expensive and environmental conditions are changing constantly. Response to oil spills is usually slow and measurement of important parameters for correlation purposes is difficult. Until recently, public opinion on field trials with small "experimental" spills has been unfavorable. Thus, inferences on the behavior of oil spills in the marine environment must be drawn from the results of laboratory-scale experiments.

Because of the complex nature of the interactions of dispersal processes, laboratory experiments simulating one dispersal process and excluding all other processes are impossible to design. Monitoring changes in the properties of the oil in the upper layer without physically perturbing the system is an insurmountable problem. In view of these limitations, the major research objectives are:

1. To investigate experimentally the spreading rates of some crude oils and petroleum products on calm water, during oil slick initiation (approximately 30 minutes);

2. To develop rate equations from experimental data determined in '1'-- important independent variables to be correlated in the equations are oil volume, viscosity, density, and surface tension. These parameters are important for determining the spreading rates of oils. They are recognized to be most desirable for correlating data;

3. To determine experimentally the dissolution rates of some crude oils and petroleum products in water - the goal is to quantitate the short-term distribution of total hydrocarbon in water following an oil spill;

4. To evaluate the performance of commercially available dispersants in emulsifying and/or solubilizing crude oils in water - the major criterion for this evaluation is the additional solubility, beyond natural dissolution, due to treatment of oils with dispersants. A detailed mechanism to explain the action of

chemical dispersants on oil slicks is to be proposed; and

5. To study the surface slick environment with respect to surface disruption, droplet formation and motion to the extent possible with available instrumentation.

The influence of factors such as temperature, water quality, environmental factors, etc. are considerable. Attempts must be made to appraise these factors.

Spreading, dissolution and chemical dispersion of oil spills are processes of significant interest in their own rights. The major reasons for exploring them lies in the belief that an increase in knowledge will assist efforts to:

a) assess the environmental impact of oil spills accurately,

b) design appropriate clean-up devices,

c) plan for contigency operations and execute plans successfully in the event of oil spillage,

d) develop sound rationales for dispersant selection and application, and

e) safeguard and protect the environment from damage caused by oil spills.

SECTION 5

LITERATURE REVIEW OF RELEVANT PREVIOUS WORK

The literature on oil pollution of the marine environment is of considerable bulk and still growing. A thorough review of all aspects of oil pollution, e.g. oil spill magnitude, legislation, containment, treatment and clean-up, forecasting, environmental effects, etc., is a major task and outside the scope of this research. Therefore, this review will be limited to the literature on the specific oil dispersal processes to be investigated. The reader is directed to several published reports (Pilpel, 1968; Blumer and Sass, 1972; Boesch et al., 1974; National Academy of Sciences, 1973a,b, 1975; Baker, 1976; Smith, 1968, Hoult, 1969; Hepple, 1971; Wolfe, 1977; Nelson-Smith, 1972; American Petroleum Institute, 1969, 1971, 1973a,b, 1975, 1977a,b, 1979) for a general overview of oil pollution of the marine environment.

The environmental impacts of spilled oil are numerous: fire hazard, fouling of beaches, damage to shore property and fishing grounds, attenuation of light and gaseous oxygen transfer between the atmosphere and aquatic biota, etc. The literature on the adverse biological effect of oil spills on marine organisms is voluminous. Because of the proliferation of assay procedures used to assess the toxicity of oily pollutants to marine life, there is disagreement on the short- and long-term effects of oil spills on aquatic biota, in spite of much published work in this area. In general, the long-term effects of oil pollution on aquatic species have neither been fully investigated nor understood. The extent to which oil is retained, metabolized or excreted following ingestion by marine fauna is not known. The National Academy of Sciences (1975) and the American Petroleum Institute (1973b, 1977b) have summarized, and documented numerous short- and long-term effects of oil spills on marine organisms. Other pertinent references on the biological effects of oil spills can be found in the general literature on oil pollution cited above. Moore and Dwyer (1974) have reviewed the literature on this subject.

Following an oil spill, several physical, chemical, mechanical and biological processes begin to act on components of the oil, as shown in Figure 1. Pilpel (1968) classified the processes into two types: dispersal and destructive. Dispersal processes include aerosol formation, evaporation, spreading, emulsification, dissolution, solubilization, sedimentation and mechanical transport by wind, wave, and current forces. Processes that dissipate oil spills include oxidation and microbial degradation. The destructive processes and some of the dispersal processes are selective, i.e. they act on certain components of petroleum. Several factors influence the extent of dispersion and destruction of oil spills: physical and chemical characteristics of the oil and environmental conditions. Important characteristics of the oil are: total volume, specific gravity, viscosity, chemical composition, type and extent of refinery treatment. Wind and current velocities, wave climate, ambient temperature, salinity, location of spill and time of the year are important environmental factors.

Some processes operate on some oil components more rapidly than others and there are numerous interactions among the processes. The interactions are so complex and poorly understood that a recent attempt to develop a mass balance model of oil spills was marginally successful (American Petroleum Institute, 1977c). An oil cycle similar to the nitrogen cycle may be considered to exist, but speculations will continue on the sinks for petroleum.

The discussions to follow focus on previous works on the spreading, and dissolution of oil slicks. Section 6 discusses chemical dispersion and emulsification.

SPREADING

Spreading of oil on water can be viewed as consisting of two parts: the natural tendency to spread on calm water in the absence of external forces and spreading as a result of mechanical transport due to wind, wave, and current forces. Both phases of spreading are important, but this section focuses primarily on the former.

As the first few drops of oil are released onto water, the oil spreads horizontally and spontaneously. This phenomenon has been observed by several investigators (Blokker, 1964; Berridge et al., 1968a, O'Brien, 1970) and is called flashing or flash spreading. Spreading occurs faster at the edges than in the bulk of the oil causing a thin film to be formed very rapidly at the water surface. The rate of spreading is rapid in the initial stages but decreases with time. Flash spreading is a function of the quantity of surface active compounds in the oil and the underlying water. All crude oils and petroleum products do not flash. For example, pure hydrocarbons usually form lenses on water (Langmuir, 1933).

One of the earliest studies of the spreading of oil is reported by Langmuir. He studied the formation of oil lenses on water by pure hydrocarbons and derived the following equation for calculating the equilibrium thickness of an oil lens:

$$h_\infty^2 = \frac{-2(\sigma_w-\sigma_o-\sigma_{ow})(\rho_w)}{g(\rho_w-\rho_o)(\rho_o)} \qquad (1)$$

where

h_∞ = the equilibrium thickness of the oil lens, cm

σ_o, σ_w, σ_{ow} = surface tensions of oil and water, and interfacial tension between oil and water, dynes/cm, respectively

ρ_o, ρ_w = density of oil and water, gm/cm^3, respectively

g = gravitational constant

Langmuir's equation was derived for pure hydrocarbons and its ability to predict the spreading behavior of crude oils and petroleum products is severely limited.

Some pure hydrocarbons spread on water. Pomerantz et al. (1967) studied the spreading behavior of low-molecular weight hydrocarbons. They found that a balance on the surface tension forces determined whether the oils spread or formed lenses. The spreading force of the oil is defined as

$$Fo = \sigma_w-(\sigma_o+\sigma_{ow}) \qquad (2)$$

where Fo is the spreading force (dynes/cm). Surface tension forces acting on an oil slick are shown in Figure 2. The oil will spread if Fo is positive. If Fo is negative, the oil will form a lens. Aging processes cause changes in σ_w, σ_o and σ_{ow}, and Fo is not constant with time. Thus, the spreading force can be positive during the initial stages of spreading and become negative during the final stages. Since Equation (1) can be written as

$$h_\infty^2 = \frac{-2Fo(\rho_w)}{g(\rho_w-\rho_o)(\rho_o)} \qquad (3)$$

the equilibrium thickness (h_∞) is undefined when Fo is positive.

The presence of indigenous surface active components in oil or water may exert a counter force against the spreading force of oils. Therefore, use of monomolecular surface films to confine spreading oil slicks has been studied by several investigators (Garrett, 1969, Garrett and Barger, 1970; Cochran and Scott, 1971; and Milz and Fraser, 1972). In the presence of an external spreading force, a modified Langmuir's equation is used to calculate the thickness of oil lenses:

$$h^2 = \frac{-2(Fo-Fm)\rho_w}{g\rho_o(\rho_w-\rho_o)} \qquad (4)$$

where

h = thickness of the oil lens, cm

Fm = external spreading force applied by the control monolayer, dynes/cm

Some spreading oils form thin continuous layers that are a few molecular diameters thick. On the sea, such oil films are responsible for the irridescent colors that are often the first tell-tale signs of oil pollution. A majority of oils do not spread into films that are continuous. Spreading oils usually break up into smaller patches and/or pools that are separated by streaks of oil-free water. Because spreading patterns are random and irregular, the final configuration for an oil slick is unpredictable. Generally, spreading causes an increase in the area covered by oil slicks beyond that expected if the oil remained stationary.

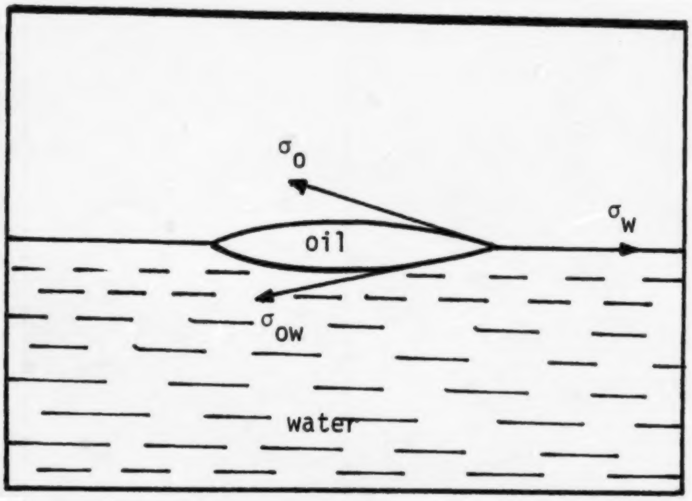

Figure 2. Surface Tension Forces Acting on an Oil Lens

Fig. 2

Blokker (1964) studied the spreading of a few oils in rectangular and circular geometries. He found that after a slick attained a mean thickness of 2 cm, the spreading rate became independent of the spreading history, but was approximately proportional to the instantaneous mean layer thickness. The following equations were derived for the rate of spreading of a homogeneous oil slick:

(a) Circular slick

$$d_t^3 - d_o^3 = \frac{24}{\pi} K_r(\rho_w - \rho_o) \frac{\rho_o}{\rho_w} V_o t \qquad (5)$$

(b) Rectangular slick

$$\ell_t^2 - \ell_o^2 = 4K_r(\rho_w - \rho_o) \frac{\rho_o}{\rho_w} \frac{V_o t}{b} \qquad (6)$$

where

$d_t(\ell_t)$ = diameter (length) of the slick at time t, cm

$d_o(\ell_o)$ = initial diameter (length) of the slick, cm

ρ_o, ρ_w = specific gravity of the oil and water, respectively

V_o = volume of the oil, cm^3

b = width of the oil slick or channel, cm

t = time, min

K_r = the Blokker coefficient, min^{-1}

Blokker observed pronounced flashing with some oils; this phenomenon was attributed to the presence of surface active components in the oils.

Berridge et al. (1968a) and Jeffrey (1971) used Blokker's equations to correlate their experimental data. Results showed wide scatter and they reported wide variations in the values of the empirical coefficient (the Blokker coefficient) determined for the oil types tested.

Fay (1969,1971) developed a theory for oil spreading on calm water. Equations that give order-of-magnitude estimates of the increase in area of an oil slick with time were developed from consideration of the forces that act on an oil slick. According to Fay (1969) there are four major forces acting on oil during spreading: gravity, viscous, inertia, and surface tension. On the assumption that oil is a homogeneous liquid with constant properties, Fay identified three distinct stages during the spreading process that depend on the major forces acting at the time. Spreading forces are balanced by retarding forces in each stage of the spreading process. The three stages and the sequence in which they occur are gravity-inertia, gravity-viscous, and surface tension-viscous. Figure 3 is a representation of the forces. Gravity and surface-tension forces tend to spread the oil, while inertia and viscous forces impede spreading.

The force of gravity causes a horizontal spreading motion of an oil slick by creating a pressure gradient between the pool of oil and surrounding water. An alternate explanation is that floating oil has an elevated center of gravity and greater potential energy. As a consequence, the lighter oil seeks a constant level and spreads sidewise, losing excess potential energy. As the oil spreads, pool thickness diminishes and the gravity force decreases. Surface tension forces act at the leading edges of the oil slick as shown in Figure 2. Table 1 summarizes the spreading equations derived by Fay for each spreading regime.

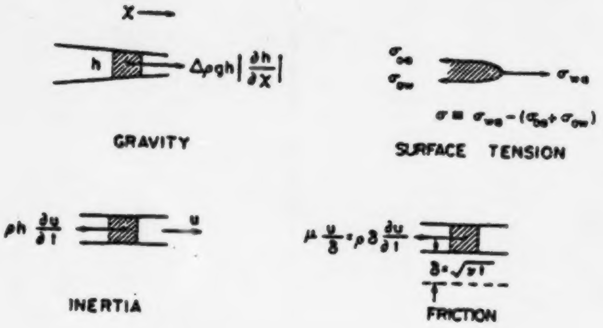
X
h
$\Delta\rho g h \left|\frac{\partial h}{\partial X}\right|$
GRAVITY
σ_{oa}
σ_{ow}
σ_{wa}
$\sigma = \sigma_{wa} - (\sigma_{oa} + \sigma_{ow})$
SURFACE TENSION
$\rho h \frac{\partial u}{\partial t}$
u
INERTIA
$\mu \frac{u}{\delta} \approx \rho \delta \frac{\partial u}{\partial t}$
$\delta \approx \sqrt{\nu t}$
FRICTION

Figure 3. The Four Forces which Act on an Oil Film during Spreading (from Fay, 1971)

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Table 1. Spreading laws for oil slicks (Fay, 1971)

Regime	One-dimensional	
Gravity-Inertia	$\ell = 1.5(\Delta g A t^2)^{1/3}$	(7)
Gravity-Viscous	$\ell = 1.5(\Delta g A^2 t^{3/2}/\nu_w^{1/2})^{1/4}$	(8)
Surface-tension-Viscous	$\ell = 1.33(\sigma^2 t^3/\rho_w^2 \nu_w)^{1/4}$	(9)
	Axisymmetric	
Gravity-Inertia	$r = 1.14(\Delta g V t^2)^{1/4}$	(10)
Gravity-Viscous	$r = 1.45(\Delta g V^2 t^{3/2}/\nu_w^{1/2})^{1/6}$	(11)
Surface-tension-Inertia	$r = 2.3(\sigma^2 t^3/\rho_w^2 \nu_w)^{1/4}$	(12)

where

$\Delta = 1-\rho_o/\rho_w$

$\sigma = \sigma_w-\sigma_{ow}-\sigma_o$, dynes/cm

ℓ, r = length and radius of the oil slick, cm, respectively

ρ_o, ρ_w = densities of oil and water, gm/cm^3, respectively

g = gravitational constant, cm/sec^2

A = volume per unit length normal to the direction of spreading, cm^2

V = total volume of oil, cm^3

ν_w = kinematic viscosity of water, cm^2/sec

$\sigma_o, \sigma_w, \sigma_w$ = surface tension of oil, water and interfacial tension between oil and water, dynes/cm, respectively

Fay (1971) contends that, as time progresses, a large spill will pass through the three stages of spreading in succession. How-

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ever, a small spill follows surface tension-viscous spreading from the start. Fay derived an equation to estimate the maximum area of an oil slick

$$A = K\left|\frac{\sigma_o^2 V^6}{\rho_w^2 \nu_w D^3 S^6}\right|^{1/8} \qquad (13)$$

where

σ_o = surface tension of oil, dynes/cm

S = solubility of the oil in water, gm/cm^3

D = diffusivity of the oil in water, cm^2/sec

K = a constant of order unity

V = volume of oil, cm^3

$\nu_w = \mu/\rho$ = kinematic viscosity of water, cm^2/sec

ρ_w = density of water, gm/cm^3

Fay (1969) extended these spreading models to account for the spread of a slick from a steady source in a moving stream. For the case of a one-dimensional slick, the following equations were derived:

Gravity-inertia $\quad \ell = (\Delta g v x^2/u)^{1/3} \qquad (14)$

Gravity-viscous $\quad \ell = (\Delta g \dot{v}^2 x^{3/2}/\nu_w^{1/2} u^{7/2})^{1/4} \qquad (15)$

Surface-tension-viscous $\quad \ell = (\sigma^2 x^3/\rho_w^2 \nu_w u^3)^{1/4} \qquad (16)$

where

$\dot{v}$ = rate of discharge of oil, cm^3/sec

x = distance from the source in the direction of flow, cm

u = water velocity, cm/sec

There is disagreement on the numerical values of the coefficients in Equations (7) through (12) (Hoult and Suchon, 1970; Fannelop and Waldman, 1971). These equations have been used to correlate experimental data for actual spills. The results appear satisfactory.

O'Brien (1970) conducted experiments on the spreading of oil on water from a stationary leaking source and found constant spreading rates after an initial time interval. Also, surface tension had a greater influence on spreading than did the gravity force.

Hoult (1972) showed that there are similarity solutions to the boundary-layer equations that predict the same results as Fay's equations.

Buckmaster (1973) studied gravity-viscous spreading and derived an expression for oil slick size as a function of time:

$$R(t) = 1.76(g\Delta)^{1/4}V^{1/2}\nu_w^{-1/8}t^{3/8} \qquad (17)$$

where R(t) is the half width of the oil slick and g, Δ, V, ν, t have been defined previously.

By solving the diffusion equation, Murray (1972) derived expressions for the maximum width and length of a slick, as a function of the concentration of oil in the water, i.e. the boundary concentration:

$$w = \frac{2Q}{(2\pi e)^{1/2}v_c C_b} \qquad (18)$$

$$\ell = \frac{Q^2}{4\pi K v_c C_b^2} \qquad (19)$$

where

w = width of the slick, cm

ℓ = length of the slick, cm

C_b = apparent boundary concentration contour, gm/cm^3

Q = rate of emission of the source, gm/sec

K = diffusion coefficient of oil, cm^2/sec

v_c = ambient current speed, cm/sec

These equations were derived based on the assumption that slick geometry is approximately elliptical. Therefore, the ratio (λ) of slick width to length and the area (A) of the slick are:

$$\lambda = \frac{4(2\pi)^{1/2} K C_b}{Q e^{1/2}} \qquad (20)$$

$$A = \frac{Q^3}{8(2\pi e)^{1/2} K v_c^2 C_b^3} \qquad (21)$$

Murray (1972) claimed his analysis is in good agreement with observations made during an oil spill.

Other investigators have studied the spreading of oil on surfaces other than water (Glaeser and Vance, 1971; McMinn, 1972; Chen et al., 1974; Chen and Charles, 1976; Weiskopf and Uzuner, 1979). The spreading history of oil on ice was found to be similar to that of oil on water, except for an additional effect due to the roughness of ice surfaces.

Chen et al. (1974) investigated the gravity-viscous spreading of crude oils on artificially prepared ice surfaces and correlated experimental data with

$$\frac{R}{V^{1/3}} = 0.24(t\rho_o g V^{1/3}/\mu_o)^{1/5} + c \qquad (22)$$

where

R = radius of the oil slick, cm

V = oil volume, cm^3

t = time, sec

ρ_o = density of the oil, gm/cm^3

μ_o = viscosity of the oil, gm/cm·sec

g = gravitational constant, cm/sec^2

c = constant

Chen and Charles (1976) studied the surface tension-viscous spreading of oil on ice and fitted experimental data with

$$\frac{A}{V^{2/3}} = KV^{(c-1)/6}(tg^{1/2}/V^{1/6})^c \qquad (23)$$

where V,c,t,g have been defined, and K is a function of oil type and temperature.

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The efforts of many investigators have increased present knowledge of the spreading of oil on water, however, all of the approaches and equations proposed to describe spreading rates of oils rely on one or more of the following assumptions:

1. the thickness of the oil is considered uniform during spreading;
2. cessation of spreading occurs when a minimal thickness has been achieved;
3. slick configuration is either rectangular, circular or elliptical throughout spreading;
4. no consideration is given to changes, with time, of physical and chemical properties of the oil and variations in composition; and
5. there is no termination of spreading.

Crude oils and petroleum products are complex mixtures of a very large number of hydrocarbons and other compounds (Rossini, 1960). Each oil component has specific properties, but the bulk oil properties are not simple functions of component properties. Oil properties vary with time from the moment the oil is spilled. The most important causes of this variation in calm water during long exposure times are the actions of weathering processes: evaporation of the lighter components of the oil mixture into the air, dissolution of the soluble components of the oil (surface active compounds, low-molecular weight hydrocarbons and polar compounds) and, possibly, emulsification of the oil components attached to highly energized surface active components. These weathering processes cause changes in oil density, viscosity and surface tension. During the latter stages of spreading, other weathering processes, e.g. bacterial degradation contribute to varying oil properties and composition (Zobell, 1969). These changes, in addition to the thinning of the oil slick, may retard and eventually stop the spreading process.

Spreading is one of the most important oil dispersal mechanisms. The extent of the surface area of the spreading oil at any time influences the rate of other dispersal processes. Thus, a thorough mathematical treatment of spreading is desirable. Because all dispersal processes are interrelated in a complex way, experimental verification of existing theories on spreading will continue pending the derivation of better models.

OIL TRANSPORT DUE TO WIND, WAVE AND CURRENT FORCES

When considering the vulnerability of a coastline and hazards to fish populations from large oil spills, the spreading characteristics of oil, particularly mechanical transport by wind, wave, and current and tidal forces are very important. The fact that oil has a calming effect on waves at sea had been known since the days of Benjamin Franklin (Giles and Forrester, 1970). But, oil pollution and, in particular, the action of these external forces did not attract research efforts until recently. Since ignorance of the interaction of these forces and oil slicks exists, a brief review of some of the significant contributions to present knowledge follows. Also, Fallah and Stark (1976a) have provided an overview and a comprehensive bibliography of many scattered publications on the movement of spilled oil at sea.

The literature is replete with studies on the effects of wind, waves and currents on transport processes at air-sea interfaces. It is clear that despite numerous observations of these phenomena, during the past two centuries, understanding has not improved significantly. Wind, waves and currents interact in a complex way and cause gross motion of water on the sea surface. In the presence of oil slicks, the influence of these forces become difficult to uncouple and to quantify.

Several investigators (Teeson et al, 1970; Schwartzberg, 1971; Warner et al., 1972; Smith, 1977) have studied the effects of wind velocities on oil slicks; it is difficult to uncouple transport due to wind from that due to waves and currents. Winds blowing over oil slicks induce several movements: oil is moved relative to the surface waters by wind-induced drift (leeway), by wind-induced surface currents (wind shear), and by wind-induced water transport. The principal motion depends on the wind velocity.

Teeson et al. (1970) experimented with circular polyethylene sheets and found drift speeds that varied from 2 to 4% of the wind speed. This range of values is in agreement with reported values of wind-induced surface drift (Wu, 1968). Other investigators have observed oil drift velocities that range from 3 to 4% of the wind speed (Smith, 1968; Nelson-Smith, 1972).

Smith (1977) determined the leeway of oil slicks and found a linear relationship between oil leeway and wind velocity:

$$v_o = 0.0179 v_w + 0.0196 \qquad (24)$$

where

v_o = oil slick leeway, knots

v_w = wind velocity 10 meters above the water level, knots

The oils that were tested drifted at approximately 3.6% of the wind speed. In the range of wind velocities studied, oil type had no significant effect on leeway.

The influence of variable wind velocities on surface drift was investigated by Warner et al. (1972). They derived model equations for the horizontal components of drift velocity for an oil patch and claimed good agreement between predictions and the observed trajectory of an actual spill.

However, there is disagreement on the direction of wind-induced oil drift. Teeson et al. (1970) measured the angles of deflection of circular polyethylene sheets drifting on water under the action of wind. Their results showed angles of deflection that varied from 0 to 20 degrees from the direction of the wind. But Murray (1975) observed an actual spill and found the oil slick to be oriented 10 to 40 degrees to the right of the local wind direction.

Since the behavior of winds can be characterized as random, Tayfun and Wang (1973) used Monte Carlo methods to simulate the movement of oil slicks by winds and currents. Two techniques were used in the simulation: random walk and time series. The models were applied to simulation of the movement and distribution of an instantaneous oil spill, with minimal success.

The combined effect of wind, wave, and current forces was investigated by Teeson et al. (1970). They concluded that oil lenses drift at a rate equal to the vector sum of the individual drift velocities. On the basis of experimental data, Schwartzberg (1971) concluded that high winds cause waves and the presence of waves reduces wind drift. He correlated the combined effect of winds and currents with

$$v_o = v_w + 0.56v_c \qquad (25)$$

where

v_o = combined drift of the oil slick, cm/sec

v_w = wind drift, cm/sec

v_c = current drift, cm/sec

Schwartzberg (1971) found that waves produced negligible small drift in the absence of wind. In the presence of wind, waves reduced the drift to about 2.7%.

In the presence of both wind-driven and tidal currents, Hoult (1972) proposed the following equation for the combined drift of the center of mass of an oil slick:

$$\frac{dx}{dt} = v_c + 0.035v_w \qquad (26)$$

where x is the coordinate of the center of mass of the oil slick, cm. Hoult accounted for the effect of wind-driven waves in the term $0.035v_w$ and suggested that additional terms be included in the equation if waves are present.

Laboratory studies (Alofs and Reisbig, 1972; Reisbig and Pottinger, 1973) have shown that the transport of oil slicks by wave-induced drift will be higher than that predicted by Stokes' theory for gravity waves.

Reisbig and Pottinger (1973) proposed two equations for wave-induced drift of oil slicks. The equations for small and large oil slicks are

$$v_o = \left(\frac{\pi H}{L}\right)^2 v_w + 0.445\left(\frac{H}{L}\right)v_w \qquad (27)$$

and

$$v_o = \left(\frac{\pi H}{L}\right)^2 v_w + 1.3\sin\left[1638\left(\frac{H}{L} - 0.005\right)\right]\cdot\left(1-e^{\frac{-\pi d}{L}}\right) \qquad (28)$$

where

v_o = oil velocity, cm/sec

v_w = wave vecocity, cm/sec

H = wave height, cm

L = wave length, cm

d = slick diameter, cm

Theoretical analysis of the motion of oil slicks under the influence of currents and wind has been presented by Shukla and Stark (1974). They considered random wind characteristics and derived a probabilistic model to describe the displacement of the center of gravity of an oil patch using a Markovian time series approach. This model was developed further by Fallah and Stark (1976b) who included wind shift at random intervals and transitional drift due to the sudden shifts in wind direction.

The subject of oil spill forecasting is growing as numerous models claim ability to accurately predict the trajectory of oil spills (Hess and Kerr, 1979). Because of diversity of assumptions in these models and the absence of accurate input data, a majority of the models are impotent. The mechanics of oil-sea interactions are poorly understood. Thus, deficiencies exist in all models and their predictive capabilities are questionable (Stolzenbach et al., 1977; Lissauer and Murphy, 1979).

In summary, waves, wind, and tidal currents cause gross motion of oil slicks and increase their areal extent over that expected for oil spreading naturally on calm water. Drifts due to tidal currents and waves are not additive, but the effect of tidal currents may be negligible because of their oscillatory nature. The effect of wind is to cause the oil to drift along the direction of the wind and to induce currents in the water column. When both wind-driven waves and tidal currents are present, complex interactions occur and quantification of individual drift rates is difficult. A simple approach involves addition of the individual drifts. Waves, wind, and tidal currents elongate and distort surface slicks. Furthermore, these forces at sea cause oil slicks to break up into patches of different sizes. The motion of each patch may become independent of the parent slick; large patches may reform and continue to be influenced by the velocity and direction of wind, waves and currents. The ultimate goal of any predictive model for the motion of oil slicks on water is a combination of the two types of oil transport processes, i.e., spreading on calm water and gross motion produced by wind, wave, and current forces.

DISSOLUTION

When oil is spilled on water, evaporation and dissolution compete for the low molecular weight hydrocarbons. Since the process of evaporation is more important during the initial stages of an oil spill, it has received more attention than dissolution. Rates of dissolution of crude oils and petroleum products are important because they influence the hydrocarbon burden that aquatic biota must bear.

Detailed studies of the dissolution rates of crude oils and petroleum products in water are scarce. Most of the work on the dissolution rates of oils in water have involved determination of aqueous solubilities of single hydrocarbons and simple mixtures of hydrocarbons. Since knowledge of the solubility of hydrocarbons in water is vital to understanding the toxicity of crude oils to marine organisms, a brief review of hydrocarbon solubilities follows.

Several investigators have studied the aqueous solubility of single hydrocarbon compounds and mixtures of hydrocarbons (McAuliffe, 1963,1966,1969a,b; Leinonen et al., 1971; Leinonen and Mackay, 1973; Sutton and Calder, 1974,1975; Eganhouse and Calder, 1976; and references cited *inter alia*).

A few investigators have tried to relate hydrocarbon solubility to some measurable property (properties) of the hydrocarbon. Bohon and Claussen (1951) found an inverse relation between solubility and molar volume for aromatic hydrocarbons. McAuliffe (1966) experimentally determined a linear relation between the logarithm of solubility and molar volume for hydrocarbons of the same homologous group. Hermann (1972) showed that, for a large number of hydrocarbons, the logarithm of solubility varies linearly with the calculated size of the solvent cavity just large enough to fit a solute molecule.

Leinonen et al. (1971) and Leinonen and Mackay (1973) proposed a correlation for predicting the solubility of hydrocarbons in water. Eganhouse and Calder (1976) studied the solubility of medium-molecular weight aromatic hydrocarbons singly and in combination. Experimental data they presented show the effects of mutual solubilities, i.e., the effect the presence of one compound has on another. Their data showed mutual decreases, mutual increases or no change in solubility.

Because solubilities reported for certain hydrocarbons are higher than values calculated based on vapor pressures and ideal solution assumptions (i.e. Henry's Law), Peake and Hodgson (1966, 1967) suggested that some hydrocarbon compounds can be "accommodated" in water. Through the process of accommodation, hydrocarbon molecules "dissolve" in water beyond usual thermodynamic solubility limits.

Factors that influence hydrocarbon solubility include pH, temperature, the concentration of dissolved salts and the presence of surface-active agents in the water column. Electrolytes in solution increase or decrease solubility by causing salting-in or salting-out of hydrocarbon molecules (McDevit and Long, 1952). Gordon and Thorne (1967a) and Eganhouse and Calder (1976) have shown that salting-out occurs in natural and artificial seawater, but the effect is fairly small. Salting-out of hydrocarbons is directly proportional to salinity. Klevens (1950) and Gordon and Thorne (1967b) found that the presence of surfactants increases the solubility of hydrocarbons, if the surfactant concentration in water exceeds the critical micelle concentration.

The molecular basis of hydrocarbon-water interactions from the perspective of the degree of aggregation of hydrocarbon molecules in water is not understood. This subject has been reviewed by Shaw (1977). Acoording to Shaw there are three degrees of aggregation:

1. true solution in the thermodynamic sense, i.e. molecularly dissolved hydrocarbon;

2. colloid and molecular aggregations less than 1 μm in size; and,

3. particles larger than 1 μm in size.

These categories are not rigidly separated and hydrocarbon species exist in a continuum from molecularly dissolved to visible particulates.

Despite the variation among the values of aqueous solubilities of hydrocarbon compounds reported by different investigators, it is widely accepted that aromatic hydrocarbons are more soluble than aliphatic hydrocarbons. The solubility of a given oil in water will depend largely on the individual solubilities of the hydrocarbon components, mutual interactions between the solubilities, the degree of accommodation, salting-in and salting-out phenomena, and the effects of natural solubilizers (surfactants) present in the water or in the oil. Low molecular-weight hydrocarbons, particularly the aromatic types, will dissolve in water rapidly; higher molecular weight hydrocarbons will be leached gradually into the underlying water, at a reduced rate. Dilution in the water column is important in determining the overall dissolution rate. The degree to which dissolution is complemented by the formation of emulsions is an important factor, also.

Several investigators have reported solubilities for crude oils and petroleum products in seawater (Boylan and Tripp, 1971; Parker et al., 1971; Smith and MacIntyre, 1971; Frankenfeld, 1973; Gordon et al., 1973; Anderson et al., 1974; Boehm and Quinn, 1974; Lysyj and Russell, 1974). Different methods were used to a) introduce the oil to water, b) equilibrate the oil/water systems, and c) measure the concentration of oil in water. The solubility values are summarized in Table 2.

The results of experiments conducted under closed static conditions will be different from those of open systems. Also, the duration of the equilibrium process has an effect on the quantity of oil dissolved in water. For example, Lysyj and Russell (1974) found an accelerated dissolution of oil into the aqueous phase after a stabilization period that lasted up to 8 days. These salient points must be considered when comparing solubility values from different studies. Unfortunately, pertinent information is not always provided.

Measurements of the concentration of oils in water under oil slicks are sparse because of the limitations of sampling. It is not an easy task to sample spatially under an oil slick without disturbing the floating oil. McAuliffe et al. (1975) measured the concentrations of dissolved hydrocarbons under controlled oil slicks in open water. The highest concentration of oil reported was 60 μg/ℓ in a sample collected 20 minutes after the spill. Spatial variation of oil concentraiions in the water could not be reported because of the sampling scheme used. Also, their samples were probably contaminated because some samples were retrieved by repeatedly dipping a steel bucket into the slick.

TABLE 2

Solubility Values for Some Crude Oils and Petroleum-Derived Products

Oil(s)	Temp. (°C)	Duration of Experiment (days)	Oil Concentration in Seawater (ppm)	Reference
Kuwait crude	23	0.5	1453[a]	Boylan and Tripp (1971)
Kuwait crude	-	36 65	400 500	Parker et al. (1971)
Three fuel oils	25	-	860[b]	Smith and MacIntyre (1971)
Venezuelan crude 1	20-25	5	6.2	Frankenfeld (1973)
Venezuelan crude 2			6.1	
Louisiana			5.9	
North African crude			8.3	
#2 fuel oil			6.5	
Bunker fuel			1.9	
Venezuelan crude and two fuel oils	19-21	7	267[b]	Gordon et al. (1973)
#2 fuel oil	23	16	9.7[c]	Lu and Polak (1973)
#2 fuel oil	23	16	7.0[c]	
Bunker oil	25	10	2.4[c]	
Crude oil	25	10	44.0[c]	
South Louisiana crude	20	0.5	19.8	Anderson et al. (1974)
Bunker C residual			6.3	
#2 fuel oil			8.7	
Kuwait crude			10.4	
#2 fuel oil	25	0.5	380	Boehm and Quinn (1974)
JP-5 fuel	25	42	110	Lysyj and Russell (1974)
DF-2 fuel			363	
Navy distillate			325	
Detergent lube oil			78	
Non-detergent lube			33	
Regular gasoline			612	
Premium gasoline			623	

[a] Aromatic species only; [b] Average value; [c] Distilled water

An oil slick is in a nonequilibrium condition with respect to dissolution and evaporation; because the latter process dominates, McAuliffe (1977) suggested that the highest concentration of oil in water should occur within the first few hours of the initiation of an oil spill.

There has been little research on the kinetics of solutions of oils into water. For open water and under static conditions, Lyons and Rideal (1929) have proposed an equation for the rate of dissolution of two immiscible liquids when one liquid (solute) is layered on the other (solvent). They assumed that the rate of dissolution is proportional to the concentration gradient and that the interface between the two liquids is saturated with the solute. The equation for the rate of dissolution is

$$\frac{dC}{dt} = D\,\frac{C_s - C}{\delta} \qquad (29)$$

where

$\frac{dC}{dt}$ = rate of dissolution of oil, gm/cm^3·sec

D = diffusion coefficient, cm/sec

C_s = oil concentration at saturation, gm/cm^3

C = oil concentration, gm/cm^3

δ = thickness of the interfacial layer between the liquids, cm (0.2 to .06 cm)

Lu and Polak (1973) studied the rates of dissolution of three oils: #2 fuel, medium bunker, and crude. They correlated experimental data with the following equation:

$$\frac{dC}{dt} = ke^{at} \qquad (30)$$

The integrated form of the equation is

$$C_\infty - C_t = kae^{at} \qquad (31)$$

where

C_t, C_∞ = concentration and maximum concentration of oil in the water per square meter of the interface, mg/liter

t = dissolution time, days

k, a = constants

The values of k and a determined by least-squares analysis are presented below:

	$k(mg/m^2)$	$a(day^{-1})$
#2 fuel oil	1043	-0.423
Crude oil	8915	-2.380
Bunker oil	459	-0.503

These experiments were conducted in closed systems and stirring was provided for the tank contents. Since oil spills occur generally in open water, the results of dissolution studies in closed tank systems cannot be considered representative of natural dissolution rates for the oils tested. Oil in open water is not in an equilibrium condition as a result of evaporation and dissolution. When dissolution studies are conducted in closed systems, evaporation of the volatile fractions of oils is reduced. These components are the soluble portion of crude oils and petroleum products. Thus, the rate of dissolution is enhanced due to the solubility of these components of petroleum that would ordinarily partition between the liquid and gas phases.

A process that is similar to the dissolution of crude oils is the rate of dissolving of monolayers. This subject is discussed in many textbooks on colloid chemistry. According to Adamson (1967), the rate of dissolution of monolayers may be considered as a single diffusion process into an infinite medium. Permeation rate (P) is given by

$$P = -\frac{d\Gamma}{dt} = C\left(\frac{D}{\pi t}\right)^{1/2} \qquad (32)$$

where

C = the bulk concentration, mg/cm^3

D = the diffusion coefficient, cm^2/sec

t = time, sec

Γ = modified concentration, mg/cm^2

The bulk concentration is assumed to be established immediately below the film in equilibrium with it. By assuming Γ is proportional to C, the equation can be integrated to yield

$$\ell n \frac{\Gamma}{\Gamma_o} = 2K\left(\frac{Dt}{\pi}\right)^{1/2} \qquad (33)$$

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where K is a proportionality constant.

Harrison et al. (1975) tried to quantify the relative rates of evaporation and dissolution within a few hours of slick initiation. They assumed the water layer immediately in contact with the oil slick is in equilibrium with the oil. Therefore, the dissolution rate can be expressed by a liquid phase dissolution mass transfer coefficient multiplied by an interfacial aqueous concentration of the oil. The rate of dissolution (R_d) was defined as

$$R_d = K_d S_i X_i \gamma_i \tag{34}$$

where

R_d = rate of dissolution, $\text{mol/m}^2\cdot\text{sec}$

K_d = mass transfer coefficient, m/sec

S_i = solubility of oil in water, mol/m^3

X_i = mole fraction of oil

γ_i = activity coefficient of oil

A value of 5.5×10^{-5} m/sec was used for the liquid phase mass transfer coefficient. This value had been suggested by Liss and Slater (1974) as a typical liquid phase mass transfer coefficient on the basis of a study of gas exchange at the air-sea interface. The analytical method used by Harrison et al. (1975) was not sensitive enough, while the sampling technique perturbed the dissolution process and the compositions of the oil and water phases.

Neely et al. (1976) proposed a mathematical model to predict concentration-time profiles for spills of chloroform onto a river. They considered the river as a series of continuously-stirred flow reactors and assumed that chloroform holdup occurs in the first reactor. Three distinct time phases were considered to account for the rate of infusion of chloroform during the accident. By writing material balance equations for each phase and for the flow of contaminant through an arbitrary compartment, a series of differential equations were derived:

$$V_n \frac{dC_n}{dt} = q(C_{n-1}-C_n)-k_e A C_n \tag{35}$$

where

C_n = concentration of oil, mg/cm^3

V_n = volume of a compartment, cm^3

q = volumetric flow of the river, cm^3/sec

k_e = rate constant for evaporation, cm/sec

A = surface area of a compartment, cm^2

n = the nth compartment ($n \geq 2$)

The parameters in the equations were adjusted during numerical integration to fit the equations to experimental data. They claimed the model was adequate for generating concentration-time profiles corresponding to data from an actual spill. This model cannot be used to predict the rates of dissolution of oil slicks in water because chloroform is heavier than water and does not form a surface slick. Similarly, the model proposed by Thibodeaux (1977) for spills of chemicals heavier than water cannot be applied to determining the rates of dissolution of oils that float on the water surface.

Rates of dissolution of oils are generally slow and should permit accurate determination. Appropriate sampling procedures must be adopted to avoid perturbing the surface slick and the underlying aqueous phase. The concentration of oil in water samples must be measured accurately, also. Duration of the equilibration period is of utmost importance. Several factors that influence the solubility of hydrocarbons in water are also important for oils. For example, the solubility of any crude oil or petroleum product will be enhanced by the presence of surface-active compounds in the oil or water (Boehm and Quinn, 1973). Emulsification and solubilization by micelle formation (Elworthy et al., 1968) may become important when seawater contains sufficient quantities of dissolved organic matter. Dissolution rates are valuable in the interpretation of laboratory bioassay experiments. They are necessary to establish whether organisms in water in close proximity to a spill will be exposed to toxic levels of oil species.

Literature on the spreading and dissolution of oil spills has been reviewed in this section. Other weathering processes act on oil and cause it to dissipate or disperse from the moment it is spilled, but this review is limited to spreading and dissolution. To conclude this section it is necessary to comment briefly on a few mathematical models that have been proposed to predict the behavior of oil spills on water.

A mathematical model of the behavior of an oil spill on water was presented by Mackay and Leinonen (1977). The model uses a simulated oil composition. Thus, the physical and chemical

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characteristics of the components in the model "oil" are known. Oil weathering processes quantified in the model are evaporation, spreading, dissolution, horizontal and vertical diffusion, and natural and chemical dispersion. Oil composition, sea state, wind speed, temperature, etc., can be varied in the model. Information generated by the model includes size and thickness of oil slick, "oil" properties and composition and the amounts of "oil" evaporated, dissolved and dispersed as a function of time after the spill. The model uses Blokker's equation (Blokker, 1964) for the rate of spreading, while the rate of dissolution of each component in the oil is given by

$$N = k(eXC_p - C_w) \tag{36}$$

where

k = dissolution mass transfer coefficient, cm/sec

e = solubility enhancement factor

X = mole fraction of oil component

C_p = solubility in water of pure component, mol/cm^3

C_w = bulk water phase concentration, mol/cm^3

The predictive ability of this model in actual spills will be limited because the derivation of the model assumes simple mixtures of hydrocarbons.

Another report (API, 1977c) presents a computer simulation model for the mass balance of oil spills. Rate equations available in the literature were used to quantify several dispersal processes in the model. Some dispersal processes were not included in the model because of lack of knowledge. Despite the complexity of this model, it cannot predict accurately the behavior of oil spills on water. Stolzenbach et al. (1977) reviewed a few models and found the predictive capability of existing models to be limited.

The fate of oil spilled on water is extremely complex to model because of the numerous processes acting to dissipate and/or disperse the oil. The marine environment is a complex system, also. Assuming that the individual rates of all weathering processes can be quantified, combination of the individual rates may not adequately describe the fate of spilled oil because of the complex interactions between the mechanisms. The behavior of crude oils and petroleum products on water will be different than simple mixtures of several pure hydrocarbons. Until accurate data from studies of individual oil weathering processes become available, mathematical models of the fate of oil spills should

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be viewed with caution. As more research is directed towards quantifying the rates of individual dispersive processes, the gap in knowledge will disappear.

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SECTION 6

CHEMICAL DISPERSION

The dispersal of oil by treating slicks with chemical dispersants cannot be understood fully without discussing briefly other relevant aspects of this subject.

OIL/WATER SYSTEMS

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When oil is mixed with water, an appreciable degree of mixing does not necessarily occur. The oil and water portions usually separate into distinct phases when the mixture is allowed to remain quiescent for a few minutes. Almost complete phase separation can occur depending on the type of oil, the volume ratio of oil-to-water, and the intensity of agitation. Complete separation of oil and water phases will not occur when the system is mixed vigorously. Because crude oils and petroleum products are slightly soluble in water, a small portion of the oil will dissolve in the water phase. Also, colloidal dispersions and oil droplets (>1 μm) will form. The formation of colloids and droplets by oils when they are mixed with water is an important mechanism for the dispersion of oil slicks.

EMULSION FORMATION

Although emulsification is treated in many textbooks on colloid and interfacial chemistry (e.g. Davies and Rideal, 1963), it is poorly understood. Only those aspects of emulsification important to the understanding of the dispersal of crude oils and petroleum products will be discussed in this section.

Crude oils and petroleum products can interact with water to form two types of emulsions: water-in-oil (w/o) and oil-in-water (o/w). A majority of crude oils have a natural tendency to form w/o emulsions (Berridge et al., 1968a,b). Stability and droplet size distributions are the most important characteristics of emulsions. Emulsions of oil-in-water are generally not stable, except when surface-active compounds are added to the system. On the other hand, w/o emulsions can be stable for long periods of time. The formation of stable w/o emulsions have been linked to

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the presence of indigeneous surface-active components in crude oils. Berridge et al. (1968b) suggested that asphaltenes and metal complexes in crude oils are responsible for the stability of w/o emulsions. Canevari (1969a) identified porphyrin compounds as promoting the formation and stability of w/o emulsions, also. Since these compounds (metal complexes, surface-active agents and porphyrins) are not present in most distillate products, these refined petroleum products do not form stable w/o emulsions. Emulsions which are stable, such as "chocolate mouse" can form tar lumps due to the action of weathering processes.

Turbulent flow conditions favor small droplet size distributions. As the oil is broken into small droplets, they are dispersed by dilution into the larger volume of seawater. The smaller the droplets, the faster they are dispersed by water movements. So emulsification can cause the concentration of oil in the water below surface slicks to exceed tolerable levels in localized areas, and cause lethal effects to aquatic biota. Water-in-oil emulsions do not mix readily with seawater. When droplets are large (>75 μm), they are no longer neutrally buoyant. In this case, the droplets may floculate and/or coalesce and rise to the surface. Oil that has coalesced may merge with the parent slick or form a separate pool of oil at the water surface. A few research studies that have increased the knowledge of emulsification are reviewed below.

The breakup of buoyant droplets in a turbulent fluid was studied by Kolmogorov (1949). The maximum stable drop size was related to flow conditions and two dimensionless parameters, the Weber and Reynolds Numbers.

Hu and Kintner (1955) experimentally investigated the splitting of oil droplets due to the density difference between oil and water phases. The following equation was used to correlate their experimental data:

$$d_{crit} = 1.452 \times 10^{-2}(\sigma_{ow}/\Delta\rho) \qquad (37)$$

where

d_{crit} = critical size of oil droplet, cm

$\Delta\rho = (\rho_w - \rho_o)/\rho_w$

ρ_o, ρ_w = density of oil and water, gm/cm^3, respectively

σ_{ow} = interfacial tension between oil and water, dynes/cm

Hinze (1955) derived an empirical correlation for turbulent emulsification, in a couette apparatus with low oil concentrations

$$d_{95} = 0.725\left(\frac{\mu_w^2}{\rho_w \sigma_{ow}}\right) \left| \frac{\mu_w^5 \varepsilon}{\rho_w \sigma_{ow}^4} \right|^{-2/5} \qquad (38)$$

where

d_{95} = diameter of the oil droplets such that 95% of the emulsions are made up of droplets smaller than this value, cm

ρ_w = density of water, gm/cm^3

μ_w = viscosity of water, gm/cm·sec

σ_{ow} = interfacial tension between oil and water, dynes/cm

ε = energy input per unit mass and time, ergs/gm·sec

The size distribution of oil particles in seawater that result from the emulsification of oil slicks has been measured under laboratory and field conditions. Gordon et al. (1973) used a Coulter Counter to determine oil particle sizes in a hydrocarbon/water system mixed under laboratory conditions. The greatest number of particles had sizes ranging from 1 to 30 μm.

Witmer and Gollan (1973) used optical techniques to measure the size distribution of oil droplets in discharged tanker ballast waters. The most frequent droplet size was about 10 μm and the smallest particle observed was 3 μm.

Lien and Phillips (1974) used a Coulter Counter to measure droplet sizes in an emulsion. The most abundant particle size was found to be slightly larger than the minimum size detectable by the instrument.

Forrester (1971) counted and measured oil particles in the water column after an oil spill from a tanker. The sizes varied from 5 to 85 μm. The number of particles with smaller sizes was greater than those with larger sizes. Forrester proposed a model to predict the probability of oil drops breaking up in a turbulent field. The model predicts a high probability for large droplets and low probability for small droplets.

There are no standard emulsion preparation methods, and different methods give different droplet size distributions. The state-of-the-art for measuring size distributions of emulsions is the Coulter Counter. This instrument is expensive and cannot be afforded by many laboratories. A major disadvantage of this equipment is the coalescence of emulsion during measurement. Thus, the final size distribution may be different from that of the original oil/water mixture. It is not surprising that few reported measurements of the size distribution of emulsions show different results.

Emulsions can be carried to subsurface depths after they are formed. When conditions are calm, the motion of small droplets ($< 1\ \mu m$) is expected to be Brownian. Larger oil droplets will rise and return to the surface slick. The rise velocity of droplets can be predicted by a modified form of Stokes' Law proposed by Bond (1927)

$$V_r = \frac{kgd^2(\rho_w - \rho_o)}{18\ \mu_w} \tag{39}$$

$$k = \frac{1 + \mu_o/\mu_w}{2/3 + \mu_o/\mu_w} \tag{40}$$

where

V_r = rise velocity of a droplet, cm/sec

d = diameter of oil droplet, cm

ρ_o, ρ_w = density of oil and water, gm/cm^3, respectively

μ_o, μ_w = viscosity of oil and water, gm/cm·sec, respectively

g = gravity constant, cm/sec^2

Under turbulent conditions, large oil droplets may be broken into smaller droplets and transported away from the center of mass of the surface slick by sea currents. Forrester (1971) found oil particles distributed as far as 250 Km from the source of an oil spill.

Fallah and Stark (1976c) developed a model to describe the diffusion of oil droplets in the underlying water using a random walk approach. The model was applied to the problem of dispersive oil losses from oil booms and a hypothetical slick was used to illustrate the model. Similarly, Leibovich (1975) developed a model to describe the turbulent dispersion of oil droplets into the water column.

Emulsification is an important process for the dispersal of oil spills. The size distribution of oil droplets is important, since the solution of hydrocarbon by molecular diffusion occurs across droplet surfaces. Emulsification is an effective dispersal mechanism for oil spills for several reasons:

1. oil droplets can be transported faster than bulk oil;
2. dissolution from droplets occurs at an accelerated pace in water masses;
3. attachment by adsorption onto suspended particles can cause sedimentation of the oil; and
4. oil droplets are small enough to be assimilated and gradually decomposed by marine organisms and bacteria.

STRUCTURE OF DISPERSANTS

Chemical dispersants are blends of surface-active compounds (or surfactants) in suitable solvent bases. The variety of chemical compounds that possess surface-active properties are so numerous that several names have been used to describe dispersants (e.g. concentrated soap solutions, detergents, solubilizers, emulsifiers, etc.). In general, surfactants are linear organic molecules containing both polar and nonpolar groups. These groups impart to the molecules their amphiphilic properties. Thus, the presence of water- and oil-soluble groups at the ends of a generally linear molecule is an important characteristic of surface-active compounds.

Poliakoff (1969) reviewed the state-of-the-art for chemicals used for dispersing spilled oil. He found that a considerable number of chemical compounds have been developed for emulsifying oil. A typical dispersant consists of a blend of surface-active compounds in aqueous, alcoholic or hydrocarbon solvent base. Usually, dispersant formulations include additives (e.g. dispersant aids, water softeners, corrosion inhibitors, etc.) to enhance efficiency. Dispersants can be divided into two groups: ionic and non-ionic. The former can be divided into two subgroups: anionic and cationic.

A surfactant molecule is often represented as a tadpole-like structure in which the "head" is water-loving (hydrophilic) while the "tail" is oil-loving (hydrophobic). Figure 4 shows some typical surfactant types: anionic, non-ionic and cationic. Anionic surfactants have structures that most closely resemble soaps (Nelson-Smith, 1972).

The chemical structure of a dispersant, particularly the ratio of oil- and water-soluble groups, is an important property. Dispersants can be classified according to the hydrophilic/lipophilic balance, also (Davies and Rideal, 1963).

There have been interesting improvements in the technology of dispersants, particularly concerning their toxicity and self-mixing properties. Dispersant technology is so advanced that

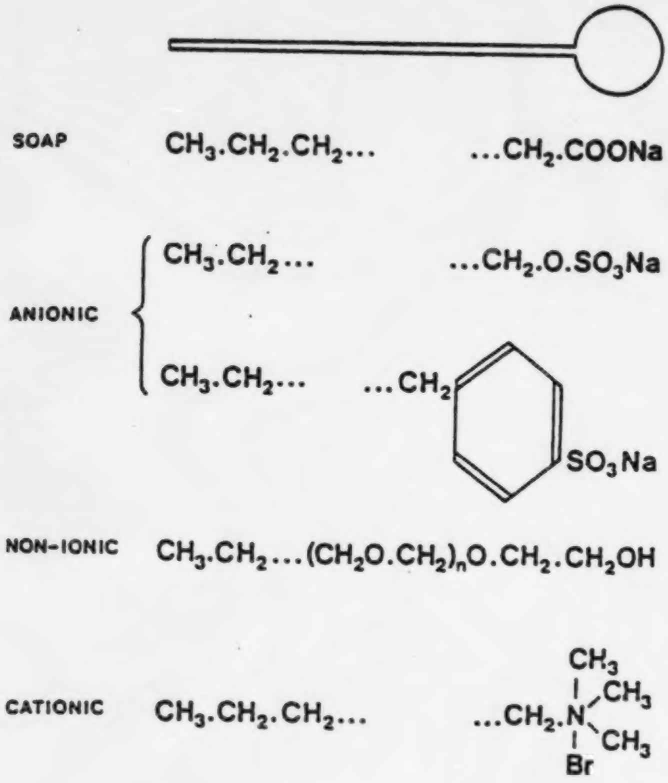

Figure 4. Some Typical Surface-Active Agents with the Lipophilic "Tail" to the Left and the Hydrophilic "Head" to the Right (Nelson-Smith, 1972)

commercial formulations may not be composed entirely of dispersants with the same chemical structure. Great variations are possible in the solvent base used to dissolve the surfactant molecules, and the chemical structure and characteristics of the dispersant.

Surface-active compounds have been found in crude oils (Siefert, 1969; Siefert and Howell, 1969). The concentration of surfactants in petroleum may be significant depending on the source and extent of refining of the crude. Corrosion inhibitors, de-icing agents and combustion promoters are blended with some petroleum products, thereby replenishing indigenous surfactants removed during refining. Seawater also contains organic compounds of both natural and anthropogenic origin that are surface-active. Sieburth et al. (1976) have shown that these materials are abundant in the surface microlayer of the sea.

COLLOID CHEMISTRY ASPECTS OF CHEMICAL DISPERSION

With turbulent mixing such as might be provided by water movements due to wind, wave, tidal, and current forces at sea, oil slicks can break up into oil droplets and disperse into the underlying water. Also, the dispersion of one liquid into another can be enhanced by modifying the interfacial tension between the two immiscible liquids.

A reduction of the interfacial tension between two immiscible liquids can cause emulsions to form. This reduction can be caused by a) adding dispersants to the oil/water system, b) pre-mixing dispersant and oil before introducing the oil into water, and c) surface-active compounds that may be present in the oil or water phase before the liquids are mixed. Surface-active compounds present in seawater (e.g. dissolved organic matter), crude oils and petroleum products enhance the emulsion-forming tendency of oil slicks. The type of emulsion dispersants form depends somewhat on whether the surfactants are preferentially soluble in the oil or water phase. Water-soluble surfactants form o/w emulsions, while oil-soluble surfactants form w/o emulsions in accordance with an empirical relation proposed by Bancroft (1915).

A surface-active compound forms aggregates called micelles in aqueous solution when the concentration of the surfactant reaches a critical value called the critical micelle concentration. The formation and properties of micelles have been discussed by Elworthy et al. (1968) and Tanford (1973). Figure 5 is a representation of a spherical micelle. Micelles have two distinct regions of dissimilar properties. In aqueous solutions, the central micro-region will dissolve hydrocarbon molecules, while the outer region is soluble in water. Thus micelles can incorporate hydrocarbon molecules into the micro-region and swell (see Figure 5). In hydrocarbon solutions, the structure of micelles is reversed, that is the hydrophilic portions of the micelles are shielded from the hydrocarbon solvent.

Colloidal particles containing amphiphilic and hydrocarbon molecules are called mixed micelles (Shaw, 1970). This phenomenon is well known as the chemical basis of detergency. The interaction of oil/water/dispersant molecules leads to a micellar type of accommodation. The resulting clusters of mixed micelles (oil droplets enclosed in thin sheets of surfactant molecules) are stable because the size distribution is in the colloidal range. Additional stability of the droplets is created by the presence of a film of surfactant molecules which protects the oil droplets and prevents coalescence by repelling droplets from one another.

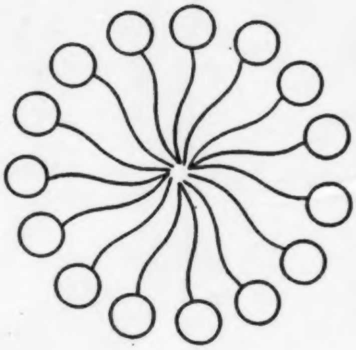

Figure 5. Schematic Representation of a Spherical Micelle (Shaw, 1970)

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VIABILITY OF CHEMICAL DISPERSION AS AN OIL SPILL CLEAN-UP METHOD

Decisions associated with public safety and ecosystem protection must be made after oil spills occur. These decisions are aimed at mitigating environmental damage to fish populations, spawning and nesting areas, shorelines, beach property, etc. The major thrust of any oil spill clean-up and control activity should be recovery of the oil. Therefore, diversion, physical containment and total recovery of spilled oil by mechanical devices are methods favored by individuals and groups concerned with preserving the environment.

Mechanical skimming devices require that oil be concentrated at the water surface for recovery to be efficient. Anchoring booms at sea poses serious problems. The length of booming equipment necessary to confine a major oil spillage presents complicated handling problems at sea. The efficient performance of booms and skimming devices is limited to sea states with waves of less than 2 feet in height and current speeds of less than 1 knot. Furthermore, logistic considerations make deployment of these devices difficult in remote areas that cannot be reached by over-land means.

Limitations on the use of containment equipment and mechanical skimmers are now widely recognized and other counter-measures have been proposed. Opinion is growing that there is a need for other spill control options, until there are improvements in the state-of-the-art for containment and removal of oil spills (Canevari, 1969b; McCarthy, 1977; McCarthy et al., 1978). Chemical dispersion of oil spills is emerging as an alternative counter-measure for large oil spills, and the proper use of dispersants for controlling oil spills has become a subject of increasing world-wide interest. The option to use dispersants to treat oil spills is attractive for several reasons.

There are circumstances when the use of booms and skimming devices may be hampered or impractical, such as with oil spills under ice, piers, jetties and docks. These areas are not easily accessible for booming, and it is impossible to use conventional recovery techniques.

In other situations, when there is a threat to life, due to fire hazard, or when beach properties and commercial fishing grounds are in danger of being impacted, dispersants may be the only means of protecting valuable areas.

Skimming equipment cannot completely recover oil slicks even when containment devices are used. It may be desirable to use chemicals to disperse the remaining oil.

The logistics of aerial application of dispersants in remote areas, not accessible by land, appear favorable (Ross et al., 1978).

Crude oils form w/o emulsions naturally. A w/o emulsion is not desirable because it coalesces readily and it is tougher than an o/w emulsion to disperse. Addition of surfactants to oil slicks enhances formation of o/w emulsions that are easily dispersable.

Finally, the volume of the oceans is tremendous and the capacity to assimilate oil droplets is infinite. These reasons support chemical dispersion as a candidate for controlling oil spills.

Damage to a coastline and marine biota from a large oil spill can be devastating. The situation can be made worse if the oil spill is localized. Mitigating the environmental damage due to oil spills is the objective of any oil spill clean-up operation. This objective can be met by careful and by controlled use of dispersants in coastal and offshore waters and in well flushed estuaries. The USEPA is aware of the need to use dispersants, under certain conditions, to protect vulnerable shoreline.

Previously, the use of dispersants posed two major problems. First, the toxicity of the first-generation dispersants was greater than that of the oils to be dispersed. The disastrous consequences to aquatic life due to toxicity of dispersant application during the Torrey Canyon spill are well documented (Smith, 1968). Since, a drastic reduction in toxicity has been achieved. A wide variety of chemical dispersants available commercially, with different surface-active components and solvent bases, are biodegradable and less toxic than their predecessors.

Another problem associated with the use of dispersants has been the energy input required to break a floating oil slick into droplets. The equation governing droplet formation is:

$$W_k = A\sigma_{ow} \tag{41}$$

where

W_k = amount of mechanical (mixing) energy or work input, ergs

A = interfacial area, cm^2

σ_{ow} = interfacial tension between oil and water, dynes/cm

A reduction in interfacial tension occurs when dispersants are added to oil/water systems, therefore the energy input required for emulsification is lower for oil/water/dispersant systems than oil/water systems. Actually, the amount of mechanical energy required to disperse oil slicks will be greater than that predicted by Equation (41). The mixing energy that is required to disperse a large oil spill may not be readily available. The turbulence created by the propeller action of a flotilla of ships has been used in some situations. Some of the newer dispersants have self-mixing capabilities (Canevari, 1973, 1975). The mechanism of action of these dispersants is similar to the diffusion and stranding mechanism that is characteristic of surfactants capable of spontaneous emulsification (Davies and Rideal, 1963). With self-mixing dispersants, it is not necessary to provide mixing energy. In this case the dispersion of oil droplets can derive energy from the motions of the underlying water column.

The application of chemical dispersants onto oil slicks to stimulate the formation and dispersion of oil droplets is a key alternative. The method is not new; dispersants were used to disperse oil during a major oil spill incident, i.e. the Torrey Canyon (Smith, 1968). Oil droplet formation and emulsification occur naturally, but to a limited extent because of the presence of surface active components in oil and in seawater. Chemical dispersion increases the natural rate of dispersion of spilled oil, and the use of dispersants is a choice between reliance on natural processes to disperse the oil and acceleration of the dispersive process by chemicals. Dispersants must be selected as the spill management alternative with as much knowledge and understanding of the mechanism of action of dispersants as possible.

LABORATORY TESTS OF THE EFFECTIVENESS OF DISPERSANTS

The literature on laboratory and field studies of dispersants is extensive. References on the subject can be found in API publications (1969, 1971, 1973, 1975, 1977a and 1979) and a special publication by the ASTM (McCarthy et al., 1978). The bulk of the published work has been on evaluation of the toxicity of dispersants on selected marine biota (API, 1973b; Renzoni, 1973; and literature cited *inter alia*). Tests in immediate response to fortuitous spills are possible, but often expensive and inconclusive.

The effectiveness of dispersants varies. Several factors influence effective oil dispersal: oil properties, characteristics of the water phase (salinity and concentration of dissolved organic matter), pH, ratio of oil-to-dispersant, method of application of the dispersant, spray drop size, contact time between oil and dispersant, temperature, dispersant structure, intensity of agitation or mixing, and environmental factors (wind and wave climates and tidal conditions). In the absence of detailed field tests, comparison tests can be performed in the laboratory under controlled conditions. Laboratory tests are necessary to assemble prior information to support selection of the best dispersant, specific to oil type and particular spill circumstances.

Since decisions to use or not to use dispersants in the field will be based in part on results of laboratory tests, it is important that laboratory tank systems and test conditions simulate actual field situations to the maximum possible extent. Because of the proliferation of methodologies, a realistic approach to chemical dispersion has been slow to evolve and claims by manufacturers have not been substantiated.

Methods used to evaluate the effectiveness of dispersants involve the application of the chemical dispersant on oil floating on water and agitation of the oil/water/dispersant mixture by means of a mechanical device. The absence of a universally accepted laboratory system and standardized testing procedures has led several laboratories to develop tests to assess the effectiveness and efficiency of chemical dispersants. Fitzgerald (1977) has listed some of the more common procedures: the Swirling Beaker, the Warren Springs Separatory Funnel, the Mobil Static Dispersion Test and the USEPA Simulated Environmental Tank Test (SET). Recently, Mackay et al. (1978) proposed a new laboratory device for performing similar tests. Because of inadequate correlation of testing procedures and variations in designs of experimental apparatus, test results may not be comparable and the performance of dispersants in the field may not be consistent with laboratory results.

In order to develop a standard laboratory system to evaluate the effectiveness of dispersants, several factors must be considered in the design of the laboratory system. These factors have been discussed by Osamor and Ahlert (1981). Also, this paper critiqued two available procedures: the SET and the Mackay Apparatus.

The kinetics of dispersant action, as well as the details of processes occurring at oil/water interfaces, are unknown. Canevari (1969a,b, 1978) has described some dispersion mechanisms. The basic function of dispersants is to break up oil slicks into tiny droplets, to help to disperse or solubilize oil into the underlying water column. A good dispersant produces an oil-in-water emulsion that is stable and has no tendency to flocculate or coalesce.

The ultimate goals of laboratory experiments are assessment of the efficiency of dispersants and an ability to extrapolate test results to predict performance during actual field use. Exact prediction of field performance is too complex, but laboratory results will give preliminary indications of how a particular crude oil or petroleum product will respond to treatment with a specific dispersant. Difficulty lies mainly in the inability to simulate in the laboratory conditions that occur in the field. Marine environments are very complex and conditions are changing constantly. Experience in the use of dispersants in the field is growing. It is important to draw from field experience for proper design of laboratory systems to evaluate the effectiveness of chemical dispersants.

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SECTION 7

EXPERIMENTAL

MATERIALS

Crude Oils and Petroleum Products

A total of 12 crude oils and petroleum products were studied. The oils had various origins and some of the oils had vague histories. Iranian crude oil was provided by the USEPA (Edison, N.J.) for this investigation. The fuel oils, i.e. #2 and #6, as well as an unidentified oil consisting of 8% crude and 92% oil derivatives, were supplied by Sun Oil (Marcus Hook, Penna.). The oil consisting of 8% crude oil was designated as 8% crude for identification purposes. The remaining eight crude oils were obtained from Mason & Hanger-Silas Mason Co., Inc., OHMSETT (Leonardo, N.J.). These crude oils are Nigerian light, Lagunillas, La Rosa (Venezuela), North Slope (Alaska), Brass River (Algeria), Suniland, Sahara and Arzew (Algeria).

The oil samples are identified and listed in Table 3. Also, Table 3 gives analytical test data on the oil samples, as performed by Mason & Hanger-Silas Mason. Measurements of some key properties (specific gravity, viscosity, surface and interfacial tensions) were made at the time the oils were received. The results of these measurements are reported in Table 4. The data of Tables 3 and 4 show good agreement; the slight discrepancies could be due to the effects of aging during storage and to differences in analytical methodology.

Sufficient quantities of the oils were procured so that all tests could be performed on samples from the same batch. All of the oils were stored in the original containers with tight caps, to prevent evaporation. Samples were withdrawn as quickly as possible and unused portions were discarded.

As there are variations in the physical and chemical properties of the oils, it is assumed that there are substantial variations in compositional characteristics because of the different origins. They represent a large fraction of oils that are transported on the oceans. Although these oils have a range of physical and chemical properties that bracket the properties

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TABLE 3

Analytical Data on Oil Samples as Performed by Mason & Hanger-Silas Mason

Oil	Specific Gravity	Viscosity (m^2/s) x 10^{-6}	Surface Tension (N/m) x 10^{-3}	Interfacial Tension (N/m) x 10^{-3}
#2 Fuel	0.864	4.96[a] 6.81[b]	32.0	28.8
#6 Fuel	0.951	2876.97[a] 6.16[b]	38.0	16.2
8% Crude	0.902	27.05[a] 9.46[b]	34.0	16.0
Iranian	0.851	10.58[a] 8.23[b]	29.2	28.4
Nigerian	0.832	7.0[c] 8.5[d]	26.0	24.2
Lagunillas	0.947	266.0[c] 17.0[d]	33.3	21.7
La Rosa Venezuela	0.905	28.1[c] 2.9[d]	31.2	26.7
North Slope, Alaska	0.892	20.0[c] 5.7[d]	28.0	20.3
Brass River, Algeria	0.813	5.8[c] 8.2[d]	26.9	25.6
Suniland	0.894	19.0[c] 7.4[d]	29.0	23.4
Sahara	0.797	5.8[c] 8.2[d]	24.7	25.2
Arzew, Algeria	0.805	5.3[c] 5.4[d]	26.2	20.7

a = 26 C
b = 83.3 C
c = 100 F
d = 210 F

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TABLE 4

Results of Measurements of Physical Properties of Oils

Oil	Specific Gravity			Kin. Viscosity (x10^{-6})[1]		Surface Tension[2]		
	21C	27C	35C	30C	35C	α_o	ow	$\sigma_{o/sw}$[*]
(H_2O)-Distilled						71.5		
- Tap	1.0	0.995	0.990			73.4		
- Salt						75.5		
#2 Fuel	0.865	0.860	0.855	3.64	3.29	30.8	28.7	26.6
#6 Fuel	0.952	0.950	0.950	2000[a]	1000[b]	37.8	23.1	22.5
8% Crude	0.905	0.902	0.895	23.71	18.99	34.7	24.1	20.8
Iranian	0.857	0.855	0.840	10.2	8.83	29.5	29.9	27.7
Nigerian	0.832	0.830	0.826	6.22	4.32	29.2	24.3	17.4
Lagunillas	0.956	0.945	0.940	1000	406.3	34.0	25.3	16.9
La Rosa, Venezuela	0.905	0.902	0.897	68.86	56.43	34.8	30.9	22.4
North Slope, Alaska	0.890	0.890	0.882	31.76	22.31	32.3	30.2	29.9
Brass River, Algeria	0.815	0.812	0.810	3.29	3.29	29.4	22.1	14.4
Suniland	0.895	0.895	0.890	21.36	20.66	31.3	26.9	26.7
Sahara	0.797	0.795	0.792	5.29	4.32	27.9	22.2	17.3
Arzew, Algeria	0.797	0.795	0.790	2.21	2.21	28.0	29.7	29.4

[1] m^2/s [2] dynes/cm [a] 37.8C [b] 40C [*] salt water (3.5% salt)

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of numerous crude oils and petroleum products, they may not necessarily reflect oils having, historically, the highest frequency of discharges into marine environments.

Chemical Dispersants

The variety of commercially available dispersants has grown rapidly with the success of research by the detergent industry. Imaginative trade names for dispersants have been encountered in the literature. Several dispersants are claimed to be able to disperse all oil slicks under different environmental conditions.

It is impossible to test all dispersants. Some dispersants were selected from the list of dispersants "approved" by USEPA. The list was compiled on the basis of commercial availability and suitability of compositional data supplied by the manufacturers. Other considerations by the USEPA, for inclusion of a dispersant in the list, are stability during storage, non-toxic effects on marine organisms, biodegradability of key constituents, and ease of application. The dispersants that were considered for testing are shown in Table 5. The characteristics of the dispersants were summarized from the manufacturers' literature. Only five of the dispersants were tested; they are referenced in subsequent discussions as Products A, B, C, D and E. These dispersants are classified below to reflect the characteristics considered during selection.

Classification	Dispersant	Product
1. Self-mix	Corexit-9527	A
2. Non-ionic		
Hydrocarbon-Solvent Base	BP 1100X	B
Aqueous-Solvent Base	Corexit 7664	C
3. Ionic		
Hydrocarbon-Solvent Base	Congo	D
Aqueous-Solvent Base	Proform TM	E

All of the dispersants were received directly from the manufacturers. Special storage was not required for any of the dispersants.

Chemicals and Glassware

All chemicals were used as purchased from the manufacturers.

Spectral grade Carbon Tetrachloride was purchased from Fisher Scientific (Cat. #C-199) and used to extract oil from water samples.

TABLE 5

Summary of Dispersants' Characteristics

Dispersant	Ionic Activity	Solvent Base =	Sp. Gr. (60 F)	Density (lb/gal) 60F	Flash Pt. (F)	Pour Pt. (F)	Viscosity (cSt) 60F	Solubility	Other Properties
Atlantic-Pacific	Non-ionic	Aqueous	1.016	8.39	No flash	21	142.4(SUS) (100F)	H_2O	pH = 9.7 Bp = 212F
BP 1100X	"	HC	0.825 (70F)	-	160-185	-	-	HC	-
BP 1100WD	"	Aqueous		7.51	126 PMOC 87 PMOC	-58C	50 (OC) 21 (21C)	H_2O	
Cold Clean	"	"	1.05	8.753	No flash	-	167.1(SUS) (100F)	H_2O	pH = 12.5 Bp = 212F
Congo Dispersant	Cationic	HC	1.0173	-	325	15	706.3(SUS) (100F)	HC	
Corexit 7664	Non-ionic	Aqueous	1.03	8.59	116	7	29 25(100F) 21(150F)	H_2O	
Corexit 8667	"	HC	0.823	6.86	172	-32	10 5(100F) 3(150F)	HC	
Corexit 9527	"	HC	1.01	8.43	172	-32	67 25(100F) 10(150F)	HC	
Gold Crew	Ionic	Aqueous			No flash			H_2O	
Proform-TM	Anionic	"	1.046	8.7		5		H_2O	pH = 9.3 (@ 1% conc)

HC = hydrocarbon

SUS = Saybolt Universal Seconds

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Nitro Fast Red B, an oil-soluble red dye was obtained from Sandoz Colors and Chemicals (East Hanover, N.J.).

Instant Ocean-Sea Salt (Aquarium Systems Co., Ohio) was used, according to manufacturer's instructions, to prepare the salt water solutions.

Granular anhydrous Sodium Sulfate (Cat. #S-421), separatory funnels, pipets, flasks, graduated cylinders, beakers, glass containers and other glasswares were purchased from Fisher Scientific.

Trimethoxysilane (3,3,3-Trifluoropropyl) was obtained from Petrarch Systems (Levittown, Pa.), and used to render glasswares and sampling tubes hydrophilic.

DATA AQUISITION DEVICES

Weight and Temperature

All weight determinations were made on a Mettler Type H6T analytical balance. The balance has a capacity of 160 grams and was manufactured by Mettler Instrument Corp. (Hightstown, N.J., Ser. #184453). Measurement can be read to the fourth decimal place.

Liquid temperatures were measured with mercury thermometers. Thermometers were calibrated in degrees Centigrade and could be read to a precision of ± 0.1 C. Thermometers were purchased from Fisher Scientific (Cat. #15-166A).

Specific Gravity

Glass float hydrometers were used to measure specific gravity. Two Fisher Scientific hydrometers (Cat. #11-510D and #11-520A) with different scale ranges were used. The first hydrometer was calibrated from 0.650 to 1.000 with 0.005 divisions, while the second had a range of 1.000 to 1.220 and 0.002 divisions.

Kinematic Viscosity

Kinematic viscosity measurements were performed using a Saybolt viscometer. The viscometer was manufactured by Precision Scientific (Chicago, Ill., Ser. #14-V-2). The device uses the capillary-tube principle for measuring liquid viscosities. The liquid is allowed to drain from the bottom of a cylinder through a short capillary tube. The time required to drain 60 ml of the liquid is recorded, in seconds using a stopwatch. Time is taken as the kinematic viscosity of the liquid. The viscosity is in Saybolt Universal seconds and can be expressed in the units,

m^2/sec, by using the following equation

$$\nu = \frac{\mu}{\rho} = (0.00237t_s - \frac{1.93}{t_s})\times9.29\times10^{-5} \qquad (42)$$

where t_s = Saybolt Universal seconds. The accuracy of kinematic viscosity measurements depends on the accuracy of the timing. Reported viscosity values are averages of triplicate measurements.

Surface and Interfacial Tension

All surface and interfacial tension measurements were made with a Fisher Scientific Model 21 Surface Tensiomat (Cat. #14-814, Ser. #1910). The manufacturer's specifications for the platinum-iridium ring (Cat. #14-812-5, #1240) are:

Mean Circumference = 5.985 cm

R/2 = 53.6135350

The Tensiomat is a torsion balance which measures the force required to pull a platinum-iridium ring free from a liquid surface (surface tension) or across the interface of two immiscible liquids (interfacial tension). To measure surface tension, the ring is submerged in the liquid and slowly raised out of the medium. As the ring is pulled from the liquid, the force necessary to separate the ring from the liquid is measured and read directly on a dial to a precision of ± 0.05 dyne/cm. For interfacial tension measurements, the ring is first submerged in the heavier liquid. Then, the lighter liquid is layered on the heavier liquid and the ring is pulled from the heavier to the lighter liquid.

The device was used in both manual and automatic mode; the results from both measurements were comparable. Triplicate measurements were made for each liquid and the results averaged. The manufacturer's manual gives details of all operational procedures and necessary corrections to the dial readings. Prior to use, the device was calibrated according to manufacturer's instructions. Usually, the surface tension of laboratory distilled water is determined first and checked for close agreement with the known value prior to sample measurements.

Infrared Spectrophotometer

To quantify the concentration of oil in water samples, infrared spectra of the samples were obtained with a Perkin-Elmer Model 599 Infrared Spectrophotometer (Ser. #113277). This equipment utilizes the double beam technique and measures the differential absorbance/transmission between two samples, i.e. a

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reference "cell" and a sample "cell". The conditions used in obtaining the spectra of all samples were wide spectral slit, scan time of 6, and chart expansion of 1.

The spectra of CCl_4-extracts of water samples were measured using matched pairs of IR grade quartz rectangular (1 cm path length) or cylindrical (5 cm and 10 cm path lengths) cuvets supplied by International Crystal Laboratories (Elizabeth, N.J.).

SETUP

This study was conducted in three phases: spreading, dissolution and chemical dispersion. A different experimental setup was used in each phase. The setups for each phase are presented separately.

Spreading Experiments

The equipment used to conduct spreading experiments is described below:

Test Tank--

The test tank is a rectangular, transparent aquarium made from 1/4-inch thick Plexiglass to facilitate visual observations. The dimensions of the tank are 5 feet long by 3 feet wide by 2 feet high. The tank was sealed against leakage with methyl chloride and a silicone rubber compound. Plexiglass bars were used to reinforce the tank at five locations at the tank walls, so it could sustain the outward hydrostatic pressure of about 200 gallons of water. Tank contents can be drained through an outlet port connected via a garden hose to a centrifugal pump.

Oil Feeding System--

There are three methods by which contaminant oil could be introduced into a receiving body of water: 1) instantaneous, 2) leakage at a constant rate, over a fixed time interval, and 3) a combination of both methods. Since method 2) is the most common method for oily discharges, a flow system was designed to feed a steady quantity of oil to the center of the test tank.

The oil feeding system consists of a variable speed Masterflex peristaltic pump, with controller, manufactured by Cole-Parmer Instrument Co. (Chicago, Ill.). The pump, which is capable of delivering 167 mls/min with no head, is used to deliver oils from a holding tank. Oil flow from the pump is directed to a specially designed feeder made out of 1/8-inch diameter stainless steel tubing. The tubing is positioned such that oil is discharged from one end of the tube located approximately 4 inches below the water surface. Thus, the oil feeding system was used to introduce the oil to be tested, beneath the water surface, at a constant rate over a fixed time.

Photographic Documentation of the Areal Extent of Spreading Oils--

The measurement of the areal extent of spreading oils is basic and essential to studies of oil transport. Conventional sequential still photography was used to document the area covered by the spreading oils. Black-and-white photographs were obtained with a Canon F-1, 35 mm single-lens reflex camera equipped with a motor drive unit. A 28 mm f/2.8, wide-angle lens was used. The camera was equipped with an interval timer and other peripherals to provide remote control capability and to sequence photographs at a selected interval. The interval timer can be preset so that the camera photographs continuously (3.5 frames per second) or varies the exposure time from 0.5 seconds to 3 minutes per frame. The camera was equipped with a film chamber which enhances the film-holding capacity of the camera to 250 exposures. Ordinary and high contrast 35 mm black-and-white films exposed through multiple filters (yellow and polarizing) were used to document the spreading boundaries of the oils investigated. The filters were used to decrease the reflectivity of the oil films and to improve contrast.

The camera was mounted directly above the test tank by attaching it to the extension arm of a Technol TC-1 copy stand. Even with this arrangement, it was not possible to locate and delineate accurately the areal extent of #2 fuel oil. In this case, the oil was dyed with an oil-soluble red dye, i.e. Nitro Fast Red B. When mixed with oils, this dye does not modify the surface tensions of the oils (Hollinger and Mennella, 1973). The quantity of the dye used was very small, but it enabled the boundaries of the oil to be identified. Surface-tension measurements of the oil and dye mixture confirmed the findings of Hollinger and Mennella (1973).

Estes and Golomb (1970) have claimed that oil on the sea surface does not image well in the spectral bands recorded by conventional black-and-white or color photography. Photographic imagery is always affected by the contrast between the object and background. To improve contrast between the spreading oils and background, the bottom of the tank was painted white. Furthermore, several flood lights were positioned at various locations such that contrast was enhanced by the angle of the light. At sea, such an arrangement would be difficult, if not impossible.

A schematic diagram of the experimental setup used to study the spreading rates of oils, is shown in Figure 6.

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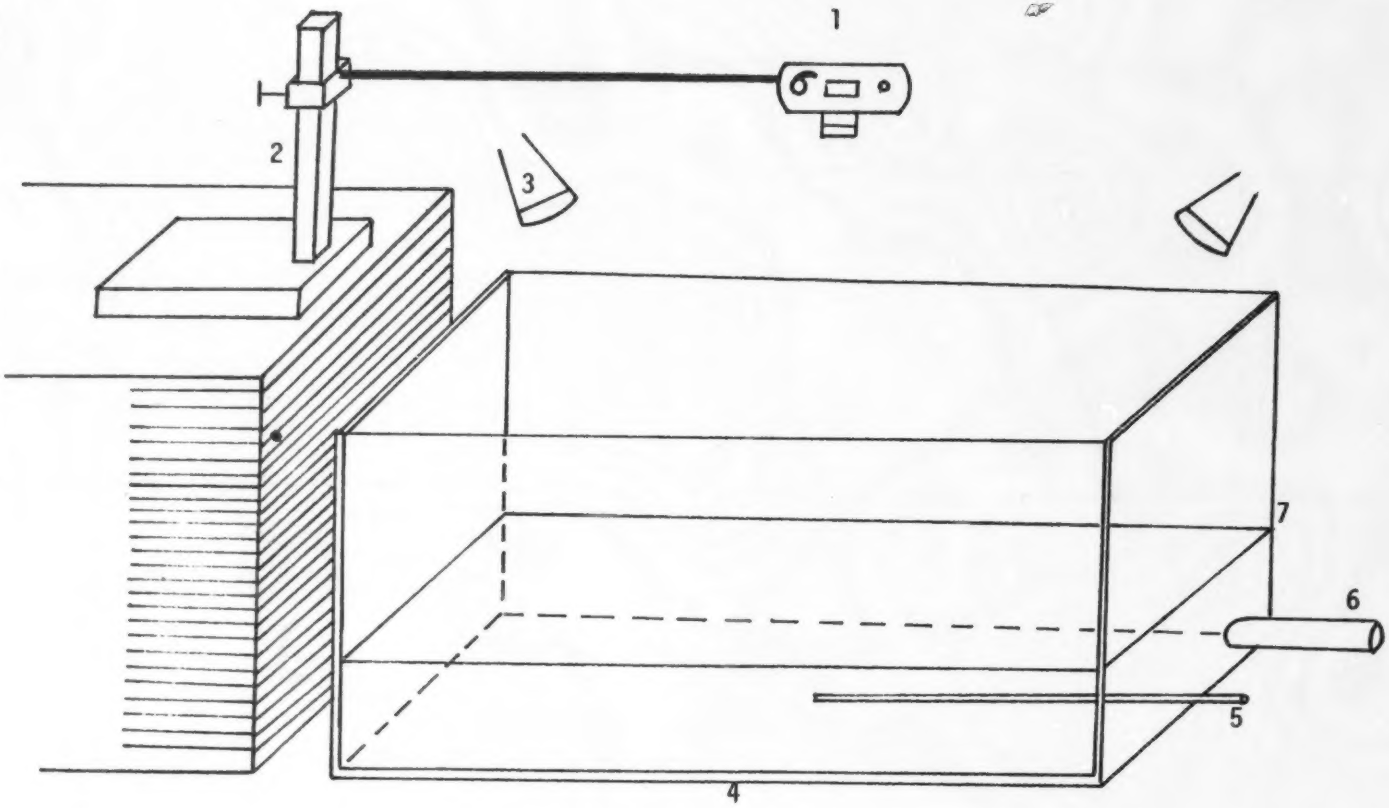

1 Programmable Camera
2 Copy Stand
3 Floodlight

4 Tank
5 Oil-Feeding Tube
6 Drain
7 Water line

Figure 6. Schematic Diagram of Experimental Setup for Spreading Studies

Dissolution Experiments

Figure 7 is a schematic diagram of the apparatus used to study the rates of dissolution of oils. It consists of a cylindrical glass tank 15 inches in internal diameter and 15 inches high.

A copper coil immersed in the tank facilitates temperature control of the water in the tank. A constant temperature thermostatic bath is used to circulate cooling water through the coil to maintain the contents of the tank at a nearly constant temperature of 25 ± 0.2 C.

Water samples are withdrawn from the tank by gravity flow through a glass tube of 1/4 inch internal diameter connected to a short piece of tygon tubing. The glass tube is located along the side of the tank such that the inlet is positioned at the center of the tank. Prior to each experiment, the sampling tube is treated to make the surfaces hydrophilic to eliminate adsorption of oil onto the tube wall. Sample withdrawals occurred with the tube positioned 6 inches from the water surface.

Chemical Dispersion Studies

The apparatus used for chemical dispersion studies is shown in Figure 8. The major components in the apparatus are the test tank, the device for applying dispersants, and the equipment for mixing the tank contents. The apparatus is discussed below. The discussion on each component also focuses on some factors that were considered during the design of the apparatus. Two setups that have gained some recognition in chemical dispersion studies are critiqued.

Test Tank--

The size of the test tank is important because it limits the volumes of water, oil and dispersant that can be used. The tank should be large enough to minimize wall surface interactions and the vertical dimension must be related to the rate of slick breakup and droplet migration. In other words, the experiment loses most of its value when droplets commence to impact the bottom of the tank and the concentration gradient reverses. If the tank size is too small, the quantity of water becomes another variable. In this case, the water/oil/dispersant ratio becomes important and the relevance of results to field situations is questionable because the quantity of water in the field is essentially infinite. The larger the tank size, the wider the variations in the quantities of oil and dispersants that can be used and the larger the volume of test water that can be maintained.

The configuration of the tank is important because of influences on the wave form. A cylindrical tank provides

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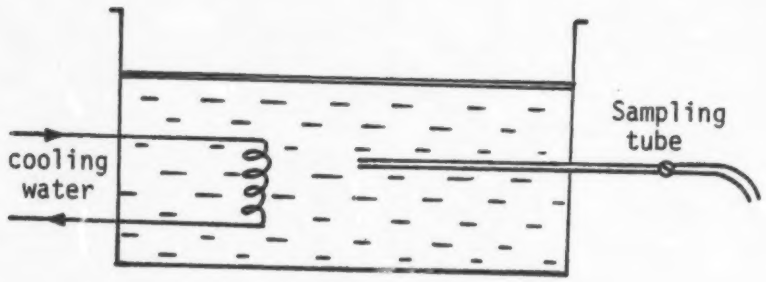

Figure 7. Schematic Diagram of Experimental Setup for Dissolution Studies

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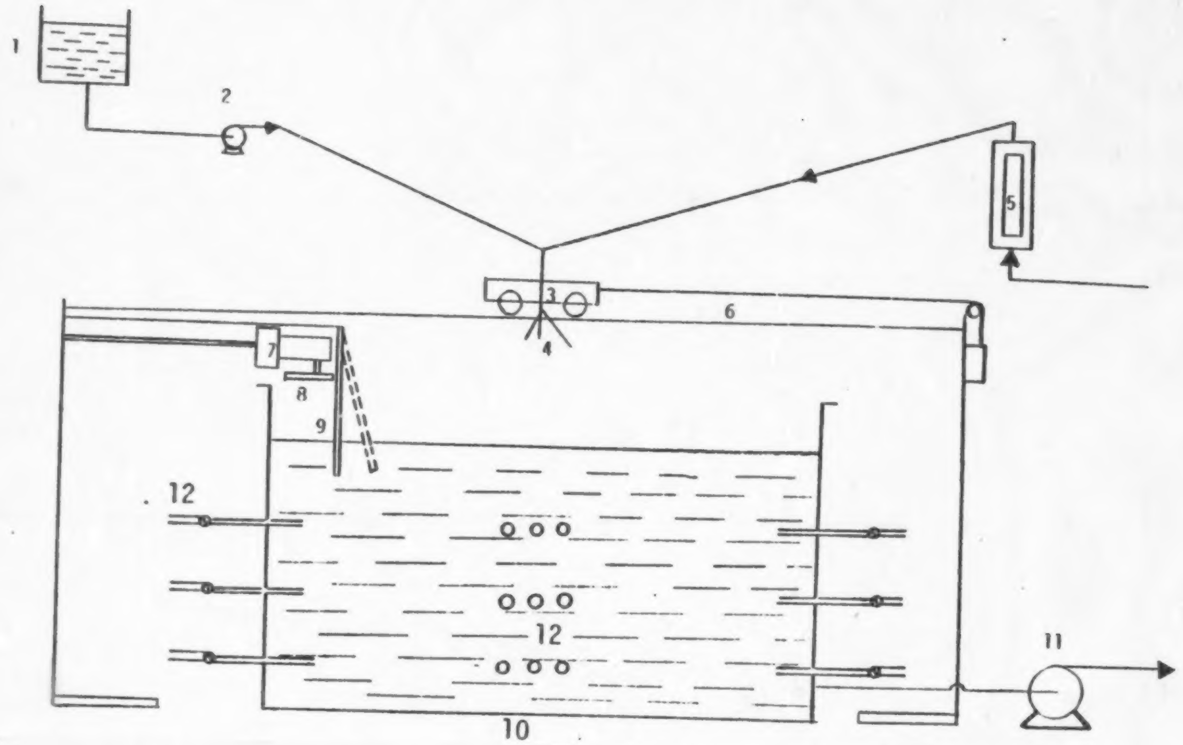

1	Dispersant Solution Holding Tank	7	Electric Motor
2	Variable Speed Peristaltic Pump	8	Eccentric Disk
3	Buggy	9	Paddle
4	Atomizer	10	Tank
5	Compressed Air Flowmeter	11	Pump
6	Rail	12	Sampling Probes

Figure 8. Schematic Diagram of Experimental Setup for Chemical Dispersion Studies

symmetry and limits variations to two spatial coordinates, however, optical measurements are difficult. Thus, the choice of a tank configuration must be predicated on measurement system selection and the device chosen to impart mixing energy.

Since hydrocarbon concentrations can be evaluated as functions of space and time, sample volume and sampling frequency are important factors determining the size of the tank. Sampling with time reduces the liquid volume in the tank but must not influence significantly the concentration gradients in the horizontal and vertical dimensions. The volume of the laboratory tank is critical for test results to be meaningful and relevant to those in the field.

Several tank systems have been used in previous investigations of the effectiveness of dispersants. For example, Murphy and McCarthy (1969) and McCarthy et al. (1973) have described the Simulated Environmental Tank (SET) system. It is a cylindrical tank, 24 inches in diameter and 28 inches high. The Mackay apparatus consists of a cylindrical glass tank 29 cm in diameter and 29 cm high (Mackay et al., 1978). Wall surface interactions will be significant due to the small volumes of these tanks.

The tank used for dispersion studies is the same as that used for spreading experiments. This tank has been described previously, but it was modified slightly by inclusion of 3/8 inch Plexiglass tubes at different locations in the tank. Sampling is accomplished by gravity flow through tubes positioned at 15 locations in the tank.

The arrangement of the sampling tubes in the tank is as follows: two adjacent vertical sides have three sampling locations each at various heights (2, 8, 14 inches) above the bottom of the tank, while a third side has the remaining tubes. The fourth side is used for visual observation. Sampling tubes are located such that water samples can be withdrawn at three depths and 6 inches from the walls of the tank. Three additional samples were generally withdrawn at three different depths but at the center of the tank.

Dispersant Application--

The effective use of dispersants requires not only an efficient material but an efficient application technique. Improper and inefficient application techniques result in unsatisfactory performance of the dispersant. For dispersants to perform at maximum efficiency, they must be applied with proper equipment. The proper application method is to spread the chemical evenly on the oil slick.

In the field, the most common methods of applying dispersants onto oil slicks are hand-held spraying equipment, fire-hoses and spray booms mounted on work boats or vessels of opportunity, e.g.

helicopters and planes. Use of hand-held sprayers is limited to small spills. For treatment of moderate and large oil spills, fire-hose systems and spray booms are necessary because of the large oil slick areas to be treated. Aerial spraying is attractive because of the possibility of application in remote areas, high dispersant dosage rates and fast response. In general, spraying equipment is designed to spray the dispersant neat (particularly for hydrocarbon-solvent-based dispersants) or to spray a dilute dispersant solution by using an eductor that feeds the chemical into a stream of seawater. Several spraying systems, including spray booms, are available commercially. Spray booms feature different nozzle arrangements; spraying height, spray size, swath area, etc. can be controlled.

At the laboratory scale, several methods have been used to introduce dispersants to treat oil:

a) mixing chemical with water prior to introducing the oil to be dispersed;
b) pouring dispersant from a container;
c) syringe injection or pipetting of dispersant into the middle of the patch of oil on water;
d) mixing dispersant with oil before pouring the mixture onto water; and,
e) spraying with hand-held spray cans.

Some of these methods, such as a) and d) are not practical in the field. These two methods will also provide maximum contact between the dispersant and oil and cause efficiencies in laboratory tests to be higher than those in the field.

The method for dispersant application in laboratory studies must reflect techniques used in the field. The method must be reproducible and characterizable. Therefore, use of hand-held spray cans or an atomizer/nebulizer is suggested. Oda (1969) described a method for applying dispersants in a fine spray on oil slicks. Application of dispersant was achieved by means of a spraying device fitted on an aerosol bomb containing a pressurized propellant. Spray cans equipped with triggers may be suitable for applying dispersants. The difficulty with using hand-held sprayers in comparative tests is the variability in hand motions and the applied pressure on the spray trigger during dispersant application. The droplet size and swath of the spray are difficult to control, also. Therefore, an atomizing system is preferred. Regardless of the method used, the dispersant must be applied uniformly and directly to the floating oil, in the form of small droplets, and not as a fog or mist.

In SET and Mackay systems, a ring is used to contain the oil slick and the dispersant is poured into the ring. In general, dispersants are used in field situations where oil slicks cannot be contained by booms due to spreading forces. Thus, the techniques for applying dispersants in both SET and Mackay systems are not valid.

Chemical dispersants were applied by an ad hoc atomizing unit. This system for applying dispersants consists of an adjustable atomizing nozzle manufactured by D. B. Smith & Co. (Utica, N.Y., Model #147). The nozzle has a general purpose setting that controls the drop size of the spray and the swath width. This type of nozzle produces a uniform flat v-shaped spray pattern instead of a hollow cone and the setting varies the size of the nozzle orifice such that "fine-to-coarse" sprays can be produced. The nozzle is connected to a short piece of metal tubing equipped with two inlets. Laboratory compressed air flows through Tygon tubing to one of the inlets. The air flow rate is monitored by a flow meter (Brooks Instrument, Hartfield, Pa., Model #1555-04C1AZZ). Dispersant solution is delivered to the second inlet by a variable-speed Masterflex peristaltic pump (Cole-Parmer, Chicago, Ill., Ser. #51526). The flow rate of dispersant solution is regulated by means of a Masterflex controller connected to the pump.

To apply a sample dispersant, compressed air and the dispersant solution are forced through the nozzle. By using different combinations of flow rates of air and dispersant, the atomizing system can produce different spray sizes and swaths.

A carriage resembling a railroad car was mounted on top of the tank to continuously reposition the atomizing nozzle. The car is positioned on a track consisting of two aluminum rods. The rods are connected to two laboratory stands so that the track crosses the tank lengthwise. The car is pulled by a fishing line attached to the rotating shaft of a low-speed gear motor (Merkle-Korff Gear Co.). This setup permits the nozzle to travel from one end of the tank to the other at a constant speed of 0.075 ft/sec to simulate the transport of a sprayer attached to a boat or plane during dispersant application in the field.

The design of the dispersant application system allows several methods of dispersant application to be evaluated. For example, the swath and droplet size of the dispersant spray can be varied by adjusting the orifice of the nozzle and varying the flow rates of air and dispersant solution. The height of the nozzle above the water level in the tank can be varied by changing the height of the track above the tank. The effects of variations in the impact velocity of dispersant sprays on oil slicks, spray angle, single and multiple passes, and spraying time per pass can be investigated with this system.

Application of Mixing Energy--

Some form of mixing or agitation must be provided to chemically treated oil slicks for complete dispersion. There is a direct relationship between mixing energy and the performance of chemical dispersants. In the field, natural wave action may provide the agitation required to disperse the treated oil. But, during calm conditions at sea, mixing energy has to be provided to disperse oil slicks even when dispersants have been applied.

Smith and McCracken (1977) and Smith (1978) have described the major methods of supplying mechanical energy to treated oil during field conditions: agitation by high pressure fire hoses, specially constructed wooden breaker-boards in tow by vessels, and turbulence produced by the propeller action of ship wakes. These methods were investigated at the OHMSETT test facility. The results of these investigations show that the efficiency of the dispersion varies according to the technique. The depth of droplet migration, and the rates of coalescence of oil droplets and slick reformation will vary for different methods. This underscores the importance of investigating different methods of supplying energy to disperse oil slicks.

When oil spills occur in remote regions, dispersants can be applied from the air but there are no means of providing mixing energy. In such cases, natural wave motions are relied upon to provide effective dispersal of the oil.

In laboratory tests, the contents of the test tank are agitated by mechanical devices, such as shakers, pumps, vortex blowers, impellers, etc. For example, the oil/water/dispersant mixture in the SET test is mixed by the shearing action of a pump. In the Mackay system, air is bubbled through the tank. Mechanical devices can create zones of dissimilar intensities of mixing, which influence the local droplet size distribution and the depth of oil droplet penetration. The stability of emulsions is a function of mechanical energy input; unstable phases will tend to remain dispersed in the presence of turbulence.

The intensity of mixing provided by laboratory devices cannot be compared with field methods for dispersing chemically-treated oil spills. The energy of agitation per unit volume of liquid in laboratory tests is likely to be much greater than under actual field conditions. Shackleton et al. (1960) studied the emulsifying characteristics of several pumps used for deballasting operations and found that stable emulsions were formed as a result of the shearing action of these pumps. It is questionable whether the mixing caused by wave motion is as intense as that provided by laboratory equipment. In the oceans, wave motions vary in a random manner, and variations occur in both space and time. Forrester (1971) measured the sizes of oil globules following a spill by the tanker Arrow and found that oil globules formed in natural wave motions were relatively large in size.

The experimental tank must be provided with means to impart mixing energy. Two devices that are well known and have been used extensively in wave studies are submersible ultrasonic transducers and wave generators of the paddle type. It is preferred to control both frequency and amplitude of mixing energy, while not physically disrupting the slick or the upper water column. An ultrasonic transducer and a wave generator meet these requirements and both have a minimum physical presence inside the tank. Also, they permit close regulation of the turbulent structure in the tank, with direct influence on incipient slick breakup and droplet motions. With these devices, the turbulence in the tank can be varied, characterized and reproduced. By using a large tank, interference from waves produced by reflection at the walls can be minimized and/or artificial wave dampeners may be used.

To impart mixing energy to the tank contents, a wave generator was designed. It consists of a paddle, made from 18 mm thick galvanized steel, that is 12 inches high and 35 inches wide. The paddle is hinged to two flexible aluminum plates, such that it is suspended vertically and dips 3 inches into the water in the tank. The paddle is capable of generating surface waves when driven by a cyclic mechanical drive. The paddle is driven by a 3-inch diameter Plexiglass disk mounted on the shaft of a high-torque, brush-type electric motor (Bodine Electric Co., Chicago, Ill., Ser. # 3424955). The disk is mounted off-center on the motor shaft to produce an eccentric sweep each half-turn.

Since the paddle was installed at one end of the tank, the system generates surface waves as the rotational force from the motor shaft is transmitted to the eccentric disk. As the disc turns, it displaces the paddle. The forward and backward movements of the paddle displace the water surface and generate waves. Contact between the paddle and the disk is maintained by two springs connected to the paddle and the tanks, one on each side of the disk.

Torque transfer from the motor to the paddle is controlled by varing the voltage to the motor using a Variac. Wave amplitude and frequency are controlled by varying the speed of the motor and the depth of paddle immersion in the water. The maximum displacement of the paddle is 1.5 inches. By allowing the system to operate for about 10 minutes, a constant wave pattern can be established in the tank. The wave pattern is reproducible and artificial devices were not used at the tank walls to dampen the waves.

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PROCEDURES

Cleaning of Glassware and Test Tanks

The capacity of oils and hydrocarbons to adsorb on surfaces is well known. In the absence of adequate cleaning procedures, the results of laboratory experiments may be biased due to artifacts from contamination of experimental apparatus. Separatory funnels for extracting hydrocarbons from thief samples, collection bottles, etc., are critical to realistic determination of oil concentrations. Thus, glassware must be cleaned thoroughly to minimize contamination of samples. Cleaning of glassware and laboratory equipment is an energy-intensive and time-consuming process in experimental studies of oil/water systems.

All glassware was washed in soap solution (Sparkleen) and rinsed in running warm tap water. Then, the glassware was extracted with acetone and carbon tetrachloride and dried in an oven at a temperature exceeding 150C. Cleaned glass containers were kept capped until used.

The plexiglass tank was cleaned by scrubbing the walls with sponge and Sparkleen soap. The tank was then rinsed with hot water from a hand-held hose. Test water was always examined for visible oil sheen before each spreading experiment. If an oil sheen was present, the cleaning procedure was repeated. For the chemical dispersion studies, the sampling tubes were disengaged and cleaned independently. At the beginning of each experiment, test water was sampled and extracted with carbon tetrachloride. If the infrared spectra of the sample indicated the presence of residual oil, the cleaning process was repeated.

Hydrophilic Treatment of Glass Surface

The spurious development of multiple phases during sampling of hydrocarbon/water systems poses great difficulty and biases determinations of oil concentrations in water samples. This phenomenon may be due to surface/oil interactions during sampling. As glass surfaces are wetted preferentially by oil, adsorption onto surfaces of sampling probes constitutes a sink for hydrocarbons when test solutions containing low concentrations of oil are sampled.

In order to minimize interactions between glass surfaces and oil, and experimental artifacts via sampling devices, it was decided to precondition the surfaces of collection bottles, sampling tubes, and separatory funnels to make them hydrophilic.

Glass surfaces were treated with trimethoxysilane to render them hydrophilic. The treatment procedure described in the manufacturer's brochure was used. It consists of a) washing the glassware with a suitable detergent, b) dipping glassware in a

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solution of trimethoxysilane for a few minutes, and c) air- or oven-drying the glassware.

The manufacturer claims that the wetting agent forms a protective film on the glassware. This film is stable to cleaning with organic solvents and solutions that have a broad pH range, for over three months.

Preparation of Seawater Solutions

Synthetic seawater solutions used in this study were prepared in batches, as required. Instant ocean sea salt was dissolved in 50 gallons of tap water in a 55 gallon drum. Complete dissolution of the salt in water was achieved by a high speed mixer. A 50 ml sample was taken from each batch and evaporated to dryness in an oven.

The salt content of these samples showed that the percent salt varied slightly for different batches; the average was approximately 3.51%. This value is in agreement with the salt content of natural seawater.

Sample Collection

Water samples were collected for analysis during experimental investigations of the dissolution and chemical dispersion of oils. Sampling can be complicated by emulsion formation or contamination. The procedure for sample collection must assure that a representative portion of the test system liquid is withdrawn.

For the dissolution studies, the first sample in each experiment was collected by means of vacuum suction. Thereafter, sampling occurred by gravity flow. The first few mls of solution that were retrieved during sampling were always discarded. This corresponds to the liquid holdup in the probe. Approximately 250 mls of sample were collected daily for analysis.

During chemical dispersion studies, samples were collected by gravity flow through the probes. Preliminary investigations showed small gradients in oil concentrations when samples from different locations in the tank were analyzed. So, a three-dimensional matrix of water samples was always collected. 50-ml samples were collected from each of the 15 locations. The samples were combined to give a sample that is representative of the tank contents.

All water samples were collected directly into separatory funnels. The funnels were stoppered immediately to prevent volatilization and changes in sample composition. Usually, samples were extracted and analyzed within 10 hours so that preservation of samples was not necessary.

Determination of Oil Concentrations in Water

Measurement of the concentrations of oil in water samples is a necessary part of most investigations of oil/water systems. The determination of hydrocarbon concentrations in water poses several analytic problems because of the very low concentrations expected for a wide range of hydrocarbons. A review of the major analytical techniques shows great diversity, but as yet no single method is a panacea for all types of problems associated with the determination of total and hydrocarbon species concentrations in water. The primary methods now available for measuring the concentrations of oil in water are spectroscopic, gravimetric, and chromatographic techniques.

Infrared spectrophotometry is the most commonly used method. The use of infrared (IR) spectroscopy to quantify the oil content of water samples is an established procedure. The method is sensitive, accurate and efficient. This technique has become popular, also, because of the short time required for analysis. But, this method is primarily for the analyses of alkanes and to a lesser extent of aromatic compounds with side chains. In this method, the oil/water sample is extracted with carbon tetrachloride (CCl_4) and the total oil content of the extract is quantified by measuring the maximum absorption attributable to methylene ($-CH_3$) stretching frequencies at 2930 cm^{-1} in 1, 5 or 10 cm path-length quartz crystal cells. Routine determinations of the total concentration of oil in water samples were made with the IR method.

Determination of the concentration of oil in water samples using the IR method has been described in detail by Gruenfeld (1977).

The procedure involves:

1. extracting oil from water samples with an organic solvent;
2. analyzing extracts with an IR spectrophotometer; and,
3. referring the maximum absorbance of the extract to a calibration curve to determine the oil content of the extract.

Gruenfeld (1977) discussed the influence of salt and acid addition to water samples, prior to extraction with the solvent, and the detection limits of oil by IR. Salt and acid were not used in the present assays.

Extraction--

Oils are soluble in most organic solvents. Spectral grade carbon tetrachloride was selected as the solvent for extracting oil from water samples for several reasons: it can be obtained in high purity, with little or no spectral interference, and it is recommended by the EPA. To extract oil from a water sample, 15 mls of CCl_4 are added to the separatory funnel containing the water sample. The funnel is stoppered and shaken vigorously by wrist action for a period of 3 minutes in an inverted position. The stoppered funnel is placed on a stand and allowed to remain undisturbed for about 1 hour. By this time, the content of the funnel has separated into two distinct phases. The bottom phase containing CCl_4 + oil is drained into a clean, solvent-rinsed bottle. The extraction is repeated on the water phase with another 15-ml portion of solvent. The extracts are combined and shaken with 2 gms of anhydrous, granular sodium sulfate (Na_2SO_4) to absorb moisture and water droplets that may be entrained in the extract. The volume of the oil-free water sample is measured using a graduated cylinder.

Infrared Analysis--

Two matched IR cells (1, 5 or 10 cm path-length) are carefully rinsed with CCl_4 and one cell, i.e. the reference cell is filled with CCl_4. The sample cell is filled with extract. The cells are placed in the IR spectrophotometer and the differential spectrum is scanned from 3200 to 2700 cm^{-1} wave numbers. The maximum absorbance of the extract is measured: it occurs at about 2930 cm^{-1}. The concentration of oil in the sample can be determined by referencing the maximum absorbance to a calibration curve of absorbance versus concentration for the cell size used. If the maximum absorbance is greater than 1.0, a smaller cell is used or the extract is diluted with a known amount of solvent. The concentration of oil-in-water is determined from the following equation:

$$C_o = \frac{C_c \cdot V_{CCl_4} \cdot f}{V_s} \qquad (43)$$

where

C_o = concentration of oil-in-water, μg/ml

C_c = concentration of oil in the extract determined from the calibration curve, μg/ml CCl_4

V_{CCl_4} = volume of CCl_4 used to extract the sample, ml f = dilution factor (if used, otherwise f = 1)

V_s = volume of water sample, ml

The instrument was checked for baseline drift regularly. CCl_4 from the same bottle was used for the extractions and for filling the reference cell. A segment from the spectra of an oil/water sample is shown in Figure 9.

Calibration Curves--

A concentration vs. absorbance plot derived from IR scans of several known concentrations of oil in CCl_4 (solvent) is used for quantitating oil in water samples. A standard solution is prepared by dissolving a weighted amount of oil into 100 ml of CCl_4. Aliquots of the standard solution are diluted with CCl_4 to obtain solutions at different concentrations. Infrared analysis of at least four solutions provides absorbance versus concentration data which is used to prepare a calibration curve for the specific oil and cell size.

The absorbance and concentration data were correlated by linear regression analysis. The correlation coefficients range from 0.98 to 1.0, indicating significant linearity. The inverse equations of the regression expressions were used to determine oil concentrations in water samples. Appendix A shows sample calibration curves for one of the oils.

Efficiency of Extraction--

The efficiency of the method that was used to extract oil from water samples depends on several factors, such as the quantity of oil in the sample, the volume of CCl_4, oil type, and the distribution of oil between CCl_4 and water phases.

Two water samples containing 0.5 and 1.0 gms of oil were prepared as follows. The oils were dissolved in 5 mls of acetone and the acetone solutions were spiked into 1 liter of water. For a control, 5 mls of acetone were spiked into 1 liter of water. The three water samples were then extracted with CCl_4, and the absorbance of the extracts determined. By subtracting the absorbance for the control from those for the samples, the quantity of oil extracted in each sample was determined. Four oils were used in this experiment: #2 fuel, #6 fuel, Nigerian crude, and Iranian crude.

In all experiments, the percent recovery was greater than 90%. The good results may be attributable to the quantity of CCl_4 used in all extractions and the hydrophilic treatment of glassware surfaces which minimizes the adsorption of oil.

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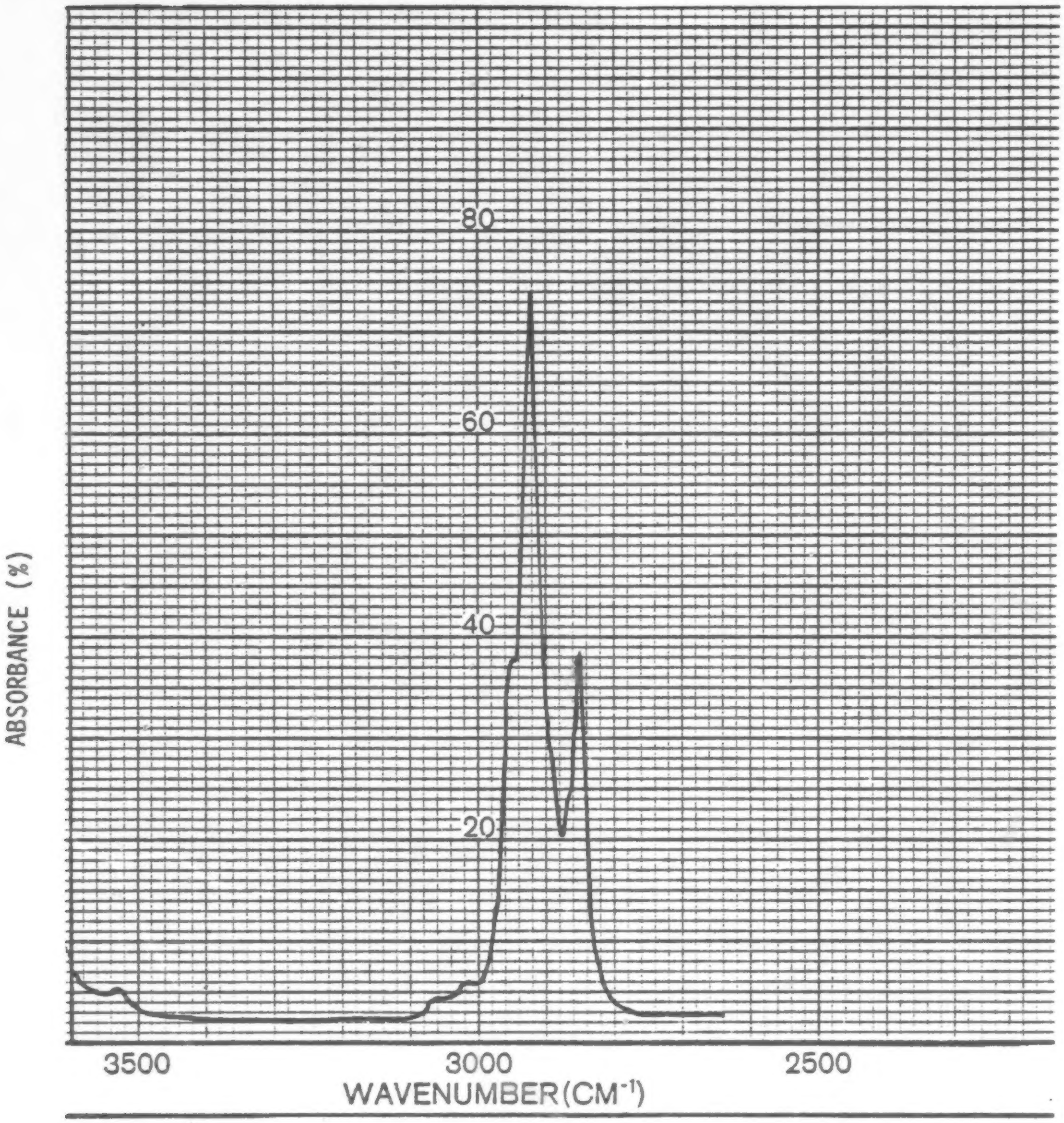

Figure 9. A Segment from the Spectra of the CCl_4 Extract of an Oil/Water Sample

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Protocol for Studying Spreading Rates of Oils on Calm Water

Experimental studies to determine the spreading rates of the 12 oils were conducted in the open, rectangular Plexiglass tank. Because of the constraint imposed by the two horizontal dimensions of the tank (5'×3'), the duration of experimental runs was limited to the first 35 minutes after slick initiation. A run was discontinued after 35 minutes or when the spreading oil contacted the sides of the tank. This was necessary to minimize wall-effects on the spreading slick.

The temperature of the tap water flowing into the tank was controlled by adjusting the flow rates of cold and hot water such that water temperature was approximately 20±1C. It was not necessary to control the temperature of the water during a run because of the short duration of the experiments.

For each oil, four different volumes (25, 50, 75, 100 mls) were spilled. Although the oils were spilled at different rates, they were discharged completely within 10 minutes.

The spreading experiments were performed according to the following procedural sequence.

1. Tank was cleaned and rinsed as described in the cleaning procedure section.

2. Tank was filled with tap water at 20 ± 1C to a depth of 12 inches. Water was checked for surface films or irridescent color. Cleaning procedure was repeated if a surface film was observed.

3. Flood lights were turned on.

4. Camera was mounted on the Technol copy stand such that the whole tank could be viewed through the view finder.

5. A circular piece of carbon paper (3.625 inches in diameter) was floated on the water surface. The camera was focused on the paper. Exposure level and shutter speed were selected to secure good contrast between paper and background. All required adjustments on camera, motor-drive, flood lights, etc. were completed.

6. The carbon paper was photographed. This served as the basis for determination of the exact magnification of photographic images of the spreading oil.

7. The oil-feeding system was installed and the volume of test oil plus an allowance for clingage was measured into the oil holding flask. The flask was connected to the oil-feeding system.

8. The peristaltic pump was turned on.

9. The stopwatch was started and the interval timer activated as soon as oil was discharged from the oil-delivery tube and rose to the water surface. The interval timer was adjusted to sequence photograph at 1 minute interval .

10. The stopwatch was stopped when the oil has been discharged completely and pertinent data recorded.

In each run, ample time was allowed for the water in the tank to become quiescent and the procedure above was standard for all the oils tested except #2 fuel oil. Because of the poor contrast of #2 fuel, a small quantity of red dye was dissolved into the oil before it was measured into the holding tank.

Determination of Oil Slick Spreading Areas--

All photographic films were developed and printed into 8"×10" prints in the dark-room facilities of the Rutgers Department of Mechanics and Material Sciences (New Brunswick, N.J.). Figure 10 shows sequence photographs of one of the spreading oils. The areas of the photographic images in the photographs were measured using a Compensating Polar Planimeter (Model #620010, Ser. #85-203), manufactured by Keuffel and Esser Co. (Morristown, N.J.).

The instrument differs slightly from a needle compass because of the presence of a tracer point and a measuring wheel connected to a vernier scale. To measure an area, the tracer point is run around the periphery of the profile from a starting (and finishing) point. As the figure is traced, the measuring wheel rotates. After a complete circuit of the figure, the distance which the wheel has revolved is determined from the difference of the initial and final readings on the vernier scale.

For each series of photographs, the area of the image of the reference carbon paper was first determined. Since the actual area of the carbon paper is known, the areas of the images of the spreading oils in the same sequence photographs could be determined. Each photograph was traced twice and the readings averaged.

The planimeter was calibrated by measuring several areas of rectangular, cylindrical and spherical geometries. From comparisons of the measured and actual areas, the precision of the instrument was deemed greater than 99%. Thus, uncertainties in measurement of actual spill areas are due largely to identification of spill boundaries as a result of poor imagery.

Accuracy of the Spreading Areas--

It was observed during the spreading experiments that the oil slicks did not spread uniformly. Regions with different thick-

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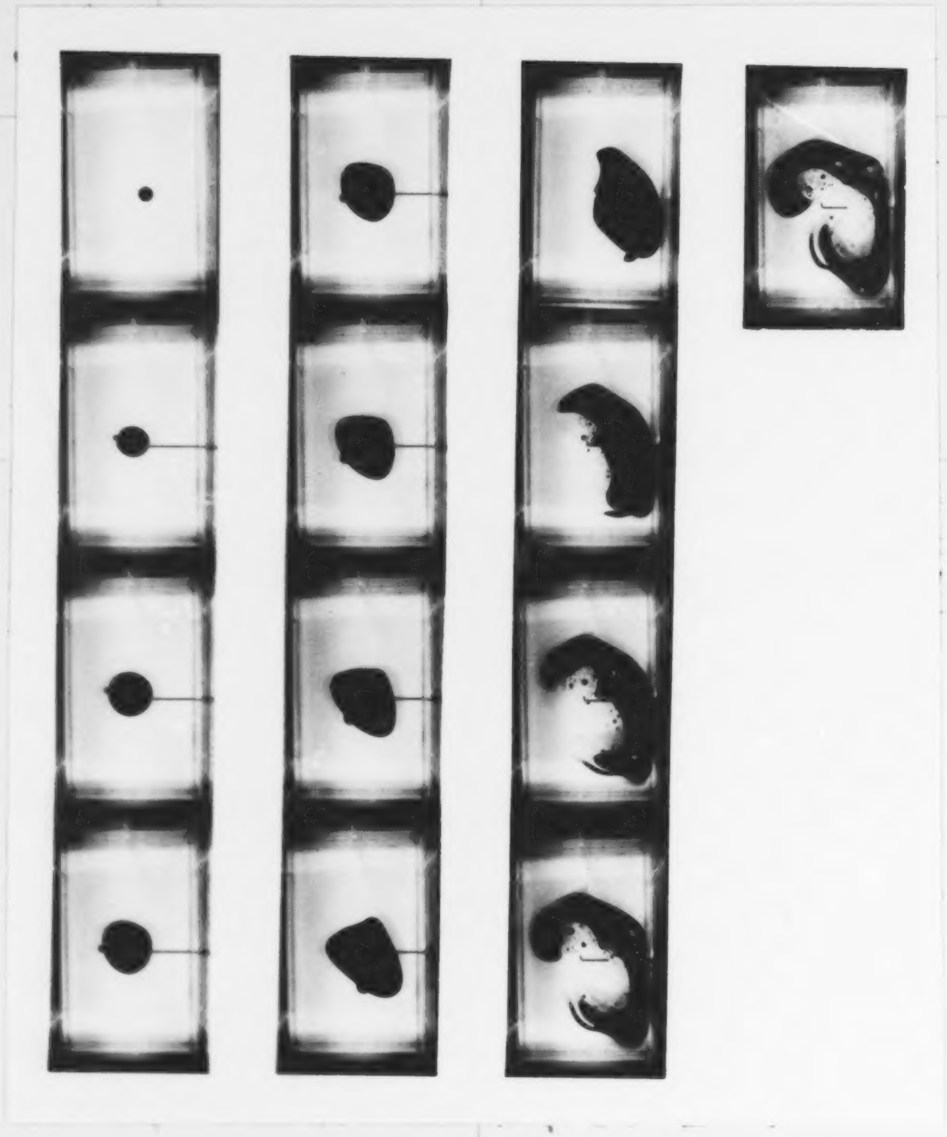

Figure 10. Sequence Photographs of Oil During Spreading

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nesses of oil were visible and appeared as different intensities in the dark color of the images when photographs were printed. Usually, darker regions were surrounded by lighter ones. Most of the oil was present in the dark regions.

The spreading patterns of the oils showed great diversity, also. Different configurations could be seen for different oil types; however, spreading patterns were more round than rectangular. A few oils spread in a circular fashion. It was not known whether the different configurations were caused by the molecular motions of water and small advection currents or by the unequal surface tension forces at the free surfaces of the oil slicks.

Situations were encountered in which the spreading oil covered the water surface within a few minutes and impacted the tank walls. Experiments were repeated in such cases. In other cases, the determination of the areal extent of spreading oil was impossible with a planimeter because spreading was not continuous. These oils usually formed fingers that were disjointed and separated by water streaks.

It was difficult to identify regions with similar contrast in all the photographs because of different spreading behaviors. Clearly, the accuracy of the spreading areas depends on the configuration and spreading behavior of the slick. For two identical experiments, the areas covered by the same oil could vary by as much as 20%. This underscores the need for a more accurate technique for determining the spreading areas of oil slicks. A color densitometer may be better suited for measuring spreading areas directly from photographic negatives.

Protocol for Studying the Dissolution Rates of Oils

The experiments to study dissolution rates of oils were conducted in three phases. In the first phase experiments, the dissolution of oils in tap water was studied. All twelve crude oils and derivatives were tested during this experimental phase. In the initial stages of the experiment, two oils (Nigerian and Iranian crudes) were equilibrated with water for three weeks. The results of these experiments showed that equilibrium was achieved in about two weeks. Therefore, the duration of subsequent dissolution experiments was reduced to two weeks.

During the second phase of experiments, the dissolution rates of only six oils in salt water were studied. Five crude oils and #2 fuel oil were tested. The crude oils are: Nigerian, La Rosa (Venezuela), Brass River (Algeria), Iranian and North Slope (Alaska). All oil/salt-water systems were allowed to equilibrate for two weeks.

Experiments using tap water and salt water were conducted in the dissolution test tank described earlier. The procedure outlined below was used for the experiments during both phases.

1. Test tank was cleaned according to the established cleaning procedure.
2. Cooling coils attached to the constant temperature bath were installed in the tank. The sampling tube was installed, also.
3. 30 liters of water (tap or 3.5% salt water) was metered into the tank.
4. Water was sampled by vacuum suction and analyzed for oil contamination. If there was contamination, the procedural sequence 1) to 4) was repeated.
5. 300 mls of oil were layered on the water by gently pouring the oil via the side of the tank.
6. The constant temperature bath was turned on.
7. The water was sampled daily for the duration of the experiment.

Prior to each sample collection, the position of the sampling probe was adjusted gently so that all samples are collected 6 inches below the oil/water interface, in the center of the cylindrical tank. The volumes of water samples collected varied from 250 to 500 mls. During sampling, precaution was taken so that the surface slick was not disturbed.

In the third phase of the dissolution experiments, concentrations at saturation were determined for all twelve oils. The procedure followed was different from that used in the first two phases. In brief, 200 mls of each oil were poured into 1-liter separatory funnels containing 500 mls of tap water. The funnels were stoppered tightly and stored in the dark for three months. After this time, 400 mls of the aqueous phase was withdrawn from each separatory funnel. Samples were extracted with CCl_4 and analyzed to determine their oil content.

It was assumed that the oil concentrations determined by this procedure would be close to the "actual" saturation values of the oils tested. The rationale in adopting this procedure stems from the fact that oil/water systems can become mutually saturated when the ratio of oil to water is close. Since oils equilibrate slowly with water, prolonged equilibration and "closed" experiments are necessary conditions for accurate determination of concentrations at saturation.

Protocol for Chemical Dispersion Studies

Although several procedures have been used to determine the effectiveness of oil spill dispersants, there is no meaningful common ground regarding acceptable procedures for evaluating dispersants.

The efficiencies of 5 dispersants were evaluated in this study. The dispersants are referred to as products A, B, C, D, and E. Three oils were treated with the dispersants. They are #2 fuel oil, Iranian crude, and #6 fuel oil. The degree of difficulty with which these oils can be dispersed varies from "easy" to "tough".

Several variables influence the effectiveness of oil spill dispersants, and it is cumbersome to evaluate all the factors, even for one oil/dispersant pair. The effects of three oil-to-dispersant dosage rates (1:1, 5:1 and 10:1 vol/vol) were studied using #2 fuel oil. The chemical dispersion of the other two oils was studied at a 5:1 oil-to-dispersant ratio only. Thus, one emphasis of this comparative study concerns the influence of oil/dispersant ratio on the effectiveness of chemical dispersants. These tests above were conducted with similar levels of agitation.

The effect of turbulence on the effectiveness of dispersants is well known. The efficiency of oil spill dispersants increases with the intensity of agitation. As some manufacturers have claimed that it is not always necessary to provide mixing energy for certain dispersants, tests were conducted with product B to determine the efficiency of the dispersion with continuous agitation and without agitation.

The effect of salt water on the dispersion of oil slicks with dispersants was also investigated with product B. Tests to determine the effects of salt water and turbulence on chemical dispersion were conducted at an oil-to-dispersant ratio of 5:1. Iranian crude and #2 fuel oil were used.

Before actual comparative tests were begun, standard procedures for dispersant application and wave generation were developed in preliminary tests.

All dispersants were atomized by pumping the dispersant solution at 2cc/sec and flowing compressed air at 375 cc/min to the nozzle. The nozzle tip was adjusted to produce a fine spray with a 9 inch swath at the water line. The railroad car (and nozzle) travels at a constant height of 18 inches above the water level. The dispersant solution is sprayed vertically downwards at a constant angle onto the oil layer and hits the water surface with a constant impact velocity. The direction of travel of the buggy is always from the downstream end of the tank (where wave breaking occurs) to the upstream end (where waves are generated).

Usually dispersants were applied in 1 pass as the nozzle travelled across the tank at a constant speed of 0.075 ft/sec. The buggy was stopped, at selected points along the tank, during application of 300 mls of dispersant in order to discharge the chemical in 1 pass.

The standard waves in all tests were generated by adjusting Variac output to 65 volts. At this setting, the eccentric disc of the wave generator makes 50 revolutions per minute. At the beginning of wave generation, waves can be seen breaking at the downstream end of the tank. After about 10 minutes of continuous wave generation, a quasi-equilibrium is established. Surface waves are random and have a characteristic amplitude of approximately 3 inches and a wave length of about 15 inches.

The procedural sequence for chemical dispersion studies follows.

1. The tank was cleaned according to the established procedure and filled with tap water to a depth of 18 inches. The temperature of the tap water was maintained at 25 ± 1C by controlling the flow rates of hot and cold water.
2. The water was sampled and the sample analyzed to determine whether residual oil was present. If necessary, the tank was cleaned again.
3. The wave generator was turned on and the setting on the Variac checked. Waves were generated for up to 10 minutes to establish a steady-state wave and current pattern in the tank.
4. 300 mls of oil were poured on the water in the tank. The oil was allowed to spread for approximately 5 minutes.
5. The volume of dispersant to be tested was measured into the dispersant holding vessel.
6. Application of the dispersant onto the oil was commenced.
7. Wave generation was stopped after 15 minutes.
8. As soon as the wave generator was stopped, approximately 50 ml samples were collected from each of the 15 sampling probes, using gravity flow. Samples were transferred into 1-liter separatory funnels for extraction and analysis.

9. Samples were collected every fifteen minutes for the first hour, and at thirty minute intervals during the next hour. Later, samples were collected twice at hourly intervals.

PRESENTATION OF EXPERIMENTAL DATA

Experimental data are presented in Appendices B to E. Appendices B and C include data for oil solubility studies in tap and salt water, respectively. All of the oils were equilibrated in tap water; only six oils were equilibrated in salt water. The experimental data for runs in tap and salt water show similar trends. The concentration of oil in water rises during the first few days; after it dropped gradually. Generally, concentration for runs in salt water were approximately an order-of-magnitude (or more) lower than runs in tap water.

Appendix D contains data for areas covered by spreading oils. Four different volumes were spilled for each oil. The experimental data shows a steady increase in area covered by any oil during the first few minutes; later, the area increased at a slower rate.

Appendix E shows the data for the chemical dispersion studies. The dispersion data for #2 fuel oil and the 5 dispersants (Products A to E) at 1:1, 5:1, and 10:1 oil-to-dispersant (O/D) ratios are given in Tables E1, E2, and E3, respectively. It can be seen that oil concentration declined throughout the sampling period, that is after the wave generator had been turned off. Also, oil concentrations are higher for high dispersant dosage rates. Tables E4 and E5 present the data for the dispersion of Iranian crude oil and #6 fuel oil, respectively. Table E6 summarizes the data for the dispersion of #2 fuel oil and Iranian crude in salt water. When this data is compared with those in Tables E2 and E4, for the same oil/dispersant pair, two conclusions can be made concerning the effect of salts. First, there were no significant differences between the data for the dispersion of #2 fuel oil in tap and salt water. In contrast, Iranian crude behaved differently in dispersion studies in tap and salt water. Table E7 compares the dispersion behavior of #2 fuel oil and Iranian crude under calm conditions and continuous agitation. The low oil concentrations in tests without agitation suggest the necessity for additional mixing energy for efficient dispersion of chemically-treated oil spills. When mixing energy is supplied continuously to disperse oil slicks, almost complete dispersion can be achieved.

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SECTION 8

MODELING OF OIL SLICK DISPERSAL MECHANICS

Mathematical models are important for advance quantitative and qualitative assessment of contamination of marine environments by oil spills. It is impossible to derive models that are valid for all oil spill situations because the rates of oil dispersal processes are site dependent. Also, the hydrodynamics of the water column under an oil slick and numerous environmental factors control the rates of oil slick dispersal processes. Since a majority of factors affecting oil dispersion cannot be quantified accurately, there is little merit in sophisticated models when accurate input data are unavailable.

In this section, simplistic models for the rates of (i) dissolution and (ii) spreading on calm water of crude oils and petroleum products are developed. A major feature of each model is the ability to fit experimental data closely. These models should provide reasonable estimates of these dispersal processes under the environmental conditions for which the models are valid. Also, the models will require as input only physical properties of the oil and water phases and other properties of the system which can be determined easily.

Finally, the mechanisms of chemical dispersion and rate expressions for some of the mechanisms will be presented. Because of the complexity of chemical dispersion processes, an overall rate expression is difficult to derive.

THE MECHANISMS OF DISSOLUTION

Discharges of oil on water masses can occur instantaneously, continuously or in a combination of both rates. In the models to be derived, it is assumed that the oil has been discharged completely before commencement of the dissolution process. Thus, the oil/water system considered here is an unlikely worst case of an oil spill, such as an oil pool which covers the entire surface of a lake or pond. This situation is different from other oil/water systems, e.g. those formed from natural seeps, as infusion and dissolution of oil occur simultaneously.

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Figure 11 shows an oil/water system in dynamic equilibrium. The system consists of three phases: air, oil and water. The thickness of the oil layer is much less than the other two phases. Regions of major interest are the air/oil and oil/water interfaces. The system may be visualized as the worst possible oil spill in a marine environment, as the oil is assumed to cover the entire water surface.

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The following mass transfer processes occur when the system is allowed to equilibrate:

a) volatile hydrocarbon evaporate at the air/oil interface;
b) hydrocarbon species diffuse from the bulk oil layer to both the air/oil and oil/water interfaces; and
c) hydrocarbon species diffuse into and dissolve in the bulk water phase.

These processes occur simultaneously and the individual rates are dependent on each other. The rates of evaporation and dissolution depend on the supply of volatile and soluble hydrocarbon species from the bulk oil. The relative rates of both processes depend on the extent to which the species partition into gas and water phases.

Before deriving the equation for the rate of dissolution of crude oils and petroleum products in water, it is useful to consider the trend of the experimental data presented in Appendix B. The data for all experimental runs show the following trends.

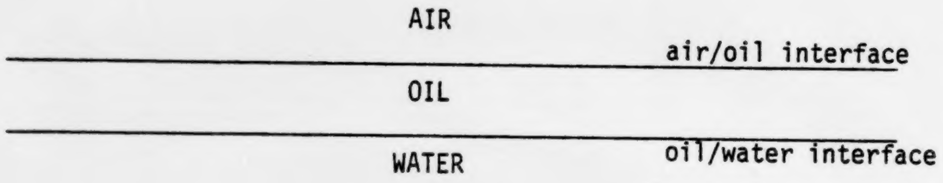

Figure 11. The Three Phases of an Oil/Water System

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At the beginning of the equilibration processes, oil concentrations in water are low but increase gradually to maximum values, within a few days. All oils did not reach maximum concentrations in water on the same day. In general, oils reached maximum solubility levels in water after approximately eight days. Oil concentrations declined gradually, during the later stages of the equilibration period.

The trend in the experimental data suggests that diffusion of hydrocarbon from the saturated oil/water interface into the bulk liquid column occurs during the early stages of the equilibration process, until the concentration of oil in water reaches a maximum. During this period, the driving force for the diffusion process is the concentration gradient, i.e. the differential concentration between the oil/water interface which is assumed to be saturated with oil and the concentration of oil in the bulk of the water column. The water column is assumed to have a uniform concentration of oil.

Movement of hydrocarbons to the oil/water interface occurs by molecular diffusion from the bulk oil layer. This transfer of soluble/volatile hydrocarbon species is necessary to "saturate" the interface but causes depletion of these materials in the bulk oil layer. Molecular diffusion of similar materials occurs from the bulk oil layer to the air/oil interface where they are lost to the atmosphere by evaporation. Thus, evaporation and dissolution processes are occurring simultaneously, but these processes may not necessarily be in equilibrium.

After maximum oil concentrations have been reached, the steady decline in concentration of oil in the water phase is caused by evaporation. Volatile hydrocarbons escape and deplete the top layers of the oil. If evaporation of hydrocarbons is to proceed, the transfer of volatile hydrocarbons from the bulk oil layer must be maintained. When the bulk oil layer is depleted of volatile hydrocarbons, diffusion of hydrocarbon to the air/oil interface continues with transfer of oil already dissolved in the water column. This is due to the greater partition coefficients of hydrocarbons with air than water. Thus, some of the hydrocarbon that evaporates at the air/oil interface is derived from the oil in aqueous solution, even though the oil may be present at a concentration which is less than saturation. The final concentration of oil during the later stages of equilibration depends on the hydrocarbon species present in each oil. Some soluble hydrocarbon species are not volatile and are retained in solution.

Formulation of the Kinetics of Dissolution

Crude oils and petroleum-based products contain organic materials that are soluble in water. Typically, these water-soluble species include hydrocarbon compounds that contain from 1 to 20 carbon atoms (C_1-C_{20}), as well as hydrocarbon compounds with nitrogen, sulfur, and oxygen molecules, and organo-metallic compounds. The complete range of soluble and volatile compounds cannot be identified for any oil type.

In order to derive an expression for the rate of dissolution of oils in water, it is important to comment briefly on the transport of materials through systems consisting of multiple phases. Several processes which involve transport of materials between layers of different phases are important in nature. For example, the exchanges of gas across air/water interfaces (Liss, 1973; Liss and Slater, 1974; Broecker and Peng, 1974), and evaporation of hydrocarbons (Mackay and Matsugu, 1973; Mackay and Wolkoff, 1973; Butler, 1975; and Cohen et al., 1978) have been investigated.

The rate of transfer of materials across interfaces can be calculated by several methods depending on the physical system and the given set of conditions. Danckwerts (1951) described several models which have been proposed to explain transport across multiple phases. The concept of stagnant films at interfaces is well entrenched in engineering literature. Also, the film theory is useful for visualizing processes at interfaces. This concept is applied here.

The air/oil and oil/water interfaces in Figure 11 are each assumed to consist of two films. For example, for the air/oil interface, it is assumed that there is a thin film of gas on the air side and a thin oil film on the oil side. Similarly, oil and water films exist on either side of the oil/water interface. Since the thickness of the oil layer formed by a majority of spills is negligible, it is convenient to visualize an oil/water system as consisting of only two films: gas and liquid films on the air and water sides, respectively. Thus, the oil layer is considered to be an extended interface separating air and water phases. The regions of an oil/water system and theoretical profiles of the oil concentrations are shown in Figure 12.

The two-film theory assumes that transport of a material from one phase to the other occurs by molecular diffusion through both films. If the transfer is a steady-state process, there is no concentration build-up in the interface and resistance to transport is due to the gas and liquid films. Gas and liquid film resistances may be considered to be in series and the rate of transfer of material is controlled by the film which offers the greatest resistance to diffusion. This theory has been used with great success to explain rates of gas transfer between air and water and evaporation of liquids. In some situations, only one of the two resistances is significant. For instance, there is no liquid film resistance during the evaporation of pure liquids because of the absence of a concentration gradient in pure liquids.

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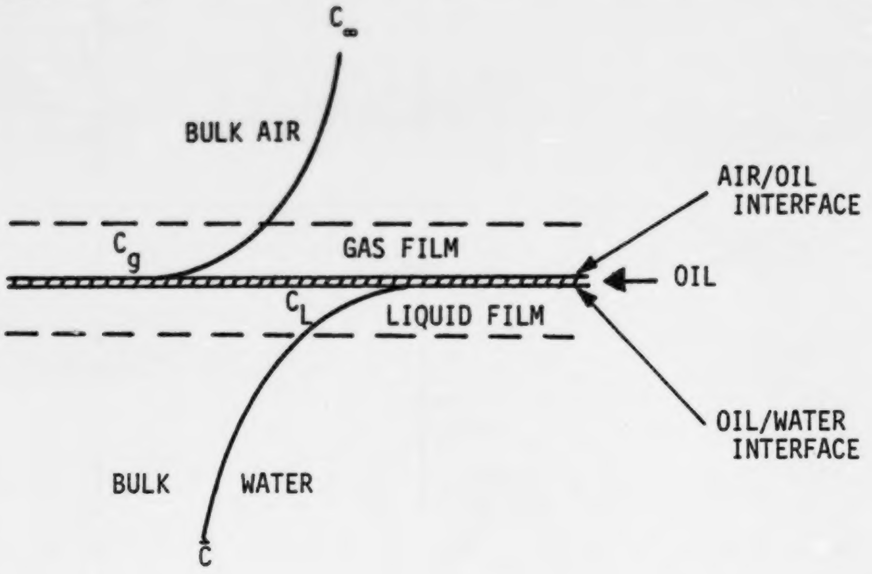

Fig 12

Figure 12. The Regions and Concentration Profiles of an Oil/Water System

For the most general case of non-steady-state transfer of a compound between two phases, the basic equation for the one-dimensional case has the form:

$$\frac{dC}{dt} = D \frac{d^2C}{dz^2} \qquad (44)$$

where

C = concentration, mg/cm^3

D = diffusivity, cm^2/day

z = direction normal to the plane across which transfer occurs, cm

t = time, days

If the transfer process occurs by molecular diffusion and steady-state conditions apply, Fick's first law is used to determine the diffusional flux in the direction of transport:

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$$F = D\,\frac{dC}{dz} \tag{45}$$

where

F = the flux of the compounds through the layer, mg/day·cm^2

D = diffusivity, cm^2/day

C = concentration, mg/cm^3

z = distance in the direction of transport, cm

Equation (45) is usually written as

$$F = k\Delta C \tag{46}$$

where

k = mass transfer coefficient or velocity of the transfer process, cm/day

ΔC = the concentration difference between the boundary surface and the average bulk concentration, mg/cm^3

Thus, the flux of a material across a layer is proportional to the concentration driving force. The magnitude of k is determined by the geometry and the flow characteristics of the system.

The experimental data suggests that the dissolution process could be divided into two parts with separate rate expressions for the solution and evaporation phases. The combined equations yield the rate of dissolution for the duration of the equilibration period.

During the early stages of equilibration when oil is dissolving in the aqueous phase, a material balance on oil in the bulk water phase is

Accumulation = Input by diffusion from the liquid film

$$\frac{d\bar{C}}{dt} = k_L\,\frac{A}{V}(C_L - \bar{C}) \tag{47}$$

where

$\frac{d\bar{C}}{dt}$ = rate of change of oil concentration in the bulk liquid phase, mg/cm^3·day

k_L = diffusivity of soluble species in the liquid, cm/day

A = interfacial area, cm^2

V = volume of liquid, cm^3

C_L = concentration of oil in the liquid film, mg/cm^3

C = average concentration of oil in the liquid phase, mg/cm^3

The interfacial area and the initial volume of liquid are known from the experimental system, but V is not constant because of loss of liquid from sample withdrawals. If it is assumed that the liquid film is saturated with oil, the rate of accumulation of oil in solution at any time is given by

$$\frac{d\overline{C}}{dt} = K_L(C_s-\overline{C}) \qquad t \leq t_m \tag{48}$$

$$\overline{C}(0) = 0 \qquad \text{(Initial Condition)}$$

where

K_L = the mass transfer coefficient $(k_L A/V)$, day^{-1}

C_s = oil concentration at "saturation" at the liquid film, mg/l

$\overline{C}$ = average oil concentration in the liquid, mg/l

Equation (48) is valid for the solution phase, that is up to some time (t_m) at which the concentration of oil in the aqueous phase is maximum. Also, it is assumed that the system is well mixed. Actually, oil concentration will vary with distance from the oil/water interface. In this study, preliminary experimental runs showed that the concentration of the sample taken 6-inches below the interface was the closest to the average value of the oil concentrations from all the locations.

During the latter part of the equilibration period, the concentration of oil in the aqueous phase decreases as a result of evaporation of hydrocarbons from solution in which the oil concentration is less than saturation. A material balance on oil in the water phase gives the rate of oil loss:

Depletion = Diffusion across the liquid film

$$\frac{d\overline{C}}{dt} = -K_L'(C-C^*) \qquad t > t_m \tag{49}$$

where C* is the oil concentration at the oil/water interface and K_L is the average mass transfer coefficient of the volatile fraction of the dissolved species. The derivation of the equation relating C^* to $\overline{C}$ follows.

The rate of evaporation of oil from solution is controlled by three resistances due to the liquid film, the oil layer, and a gas film. The resistance to diffusion due to the oil layer is negligible because of the small distance the volatile species travel. If there is no accumulation in the oil layer, the rate of diffusion of volatile species from solution is in equilibrium with the rate of evaporation at the air/oil interface. Under steady-state conditions, Fick's first law is applied to the liquid and gas phases to determine the diffusional flux in the direction of transport

$$K_L'(\overline{C}-C^*) = K_g(C_g-C_\infty) \tag{50}$$

where K_L', K_g = liquid and gas mass transfer coefficients, day^{-1}, respectively

$\overline{C}, C^*, C_g, C_\infty$ = concentrations of volatile/soluble species in liquid bulk, in the liquid at the interface, in the gas at the interface, and in bulk air, mg/l, respectively

The interfacial concentrations can be related by an empirical equation of the form

$$C_g = K_H C^* \tag{51}$$

Equation (51) is similar to Henry's Law, where K_H is the Henry's Law constant or the partition coefficient of the volatile species in gas and liquid phases.

The concentration of these materials in air, C_∞, is negligible. Substituting for C_g in Equation (50) and eliminating C_∞ gives

$$K_L'(\overline{C}-C^*) = K_g K_H C^* \tag{52}$$

Solving for C^* in Equation (52) and substituting the result into Equation (49), gives

$$\frac{d\overline{C}}{dt} = -K_E\overline{C} \qquad t > t_m \tag{53}$$

$$\overline{C}(t_m) = \overline{C}_m \qquad \text{(Initial Condition)}$$

where

$$\frac{1}{K_E} = \frac{1}{K_L'} + \frac{1}{K_g K_H} \tag{54}$$

and $\overline{C}_m$ = maximum concentration attained at time equal t_m, mg/l.

The duration of the equilibration period determines which of the two processes, i.e. solution or evaporation, is operative. Equations (48) and (53) jointly give the rate of dissolution. The lag period between the transfer of oil into water and the beginning of evaporation from solution is accounted for by using different integration limits for the two equations.

Actually, these equations are for individual hydrocarbon species that are volatile and soluble. Thus, the final expressions should be summations over all volatile and soluble species. Crude oils and petroleum products contain numerous compounds with varying solubilities and volatilities. It is an impossible task to identify completely all the compounds in any given oil that dissolve into water and later evaporate from solution. The analytical method used in this study measures only the total concentration of extractable organics.

If the mass transfer coefficients are assumed constant, integration of Equations (48) and (53) and substitution of the initial conditions gives

$$\overline{C} = C_s(1-e^{-K_L t}) \qquad (t \leq t_m) \tag{55}$$

and

$$\overline{C} = \overline{C}_m \exp[-K_E(t-t_m)] \qquad (t > t_m) \tag{56}$$

where

$$C_m = C_s(1-e^{-K_L t_m}) \tag{57}$$

The dissolution equations can be considered as a segmented model with a joint point at t_m. If the equilibration period is less than t_m, Equation (55) gives the variation of oil concentration as a function of time of equilibration. If the oil/water system is allowed to equilibrate beyond t_m, the concentration of oil in the liquid phase varies with time according to Equation (56).

THE RATE OF OIL SPREADING ON CALM WATER

It is impossible to predict accurately the rate of spreading of an oil slick. Spreading rates are site dependent and are influenced by the hydrodynamics of the underlying water and surface air columns.

A few theoretical studies which have improved the knowledge of oil slick transport have been reviewed. More recent experimental investigations have involved actual field studies in which large volumes of oil have been spilled intentionally at sea. The costs associated with such studies are exorbitant and the information derived from actual field tests may be relevant only to specific spill situations.

Usually, the spreading of oils on water is considered to consist of two independent mechanisms (Hoult, 1972). The first mechanism is the tendency of the oil to spread as a gravity wave on calm water; the second mechanism comprises the gross transport of oil masses in the presence of external forces, i.e. the convective forces of winds, currents, tides and waves. The total area covered by an oil spill is a combination of the areas covered by both spreading mechanisms. Knowledge of oil transport by convective forces at sea is improving because of increasing observations of actual spills.

Two approaches have emerged from previous work for dealing with the spreading of oils on calm water. A most significant contribution was made by Fay (1969, 1971), who proposed three stages during the spreading history of oil slicks on calm water for oils discharged instantaneously. Each stage is a balance between a retarding and a spreading force.

Using a different approach, Murray (1972) derived an expression for the area covered by an oil slick from the solution of the one-dimensional Fickian diffusion equation. Fannelop and Waldman (1971), Hoult (1972) and Buckmaster (1973) showed that expressions similar to Fay's can be derived by solving the basic equations for describing movement and mixing of a contaminant, i.e., continuity and momentum equations, with specific boundary conditions.

The approach used by Fay is better from the standpoint of ease of estimation of the areal extents of oil slicks on calm water. This method is adopted here. The goal is to develop expression(s) that permit prediction of areal increase with time, for an oil slick spreading from a stationary source, using as input data only the limited information available at a spill site. This information includes an estimate of the total volume of oil spilled, duration or rate of spill, and the physical properties of the oil and water, i.e. viscosity, density, surface and interfacial tension.

Assumptions are that:

a) physical properties of oil and water phases do not vary with time;
b) the thickness of the oil layer is always smaller than the horizontal dimensions of the slick; and
c) oil is discharged onto water at a relatively constant rate.

The first assumption is only valid during the initial stages of spreading. Since the experimental spreading studies lasted only 35 minutes, changes in the physical and chemical properties of oil and water phases were not considered significant. In general, weathering processes operate on oil slicks and cause changes in oil composition. Evaporation causes volatile components of the oil to be lost to the atmosphere and dissolution causes soluble components to leach into water. The effects of other weathering processes, e.g. microbial degradation, photo-oxidation, etc., may be significant also, depending on the duration of oil exposure. Density and viscosity of oil increase with time but the net value of the surface tension balance may be positive or negative at any instant. The second assumption is necessary if the oil is to be in hydrostatic equilibrium in the vertical dimension.

Formulation of Spreading Equations

Figure 13 is a schematic diagram showing an oil slick on water. The thickness (h) of the slick varies with time, t. The oil floats a height Δh above the mean water surface. If the flowrate of oil onto water, Q, is assumed to be fairly constant then

$$V = Qt \qquad t \leq t_D \tag{58}$$

$$V = V_t \qquad t > t_D \tag{59}$$

where

V = volume of oil, cm^3

V_t = total volume spilled, cm^3

Q = volumetric oil flowrate, cm^3/sec

t = time, sec

t_D = duration of oil spill, sec

If exchanges of oil at the free surface boundaries of the slick due to evaporation and dissolution are negligible, conservation

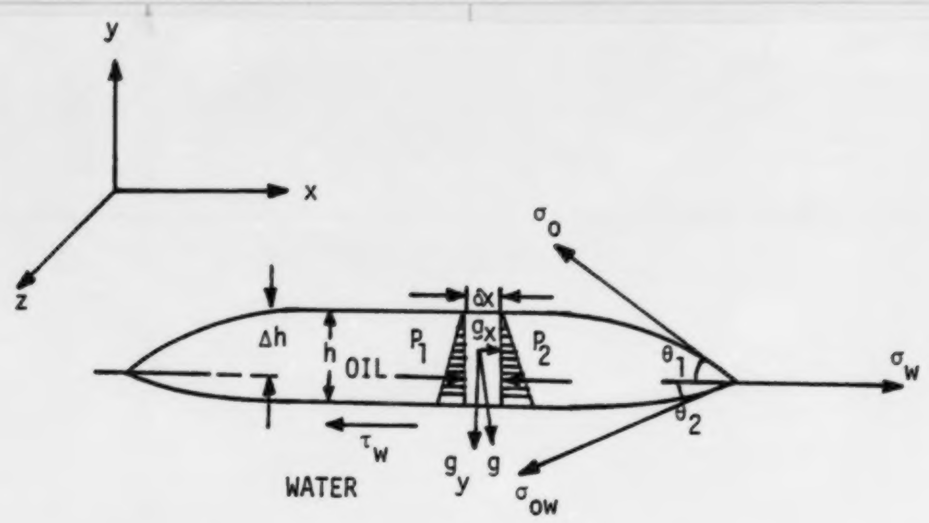

Figure 13. Schematic Diagram of an Oil Slick on Calm Water Showing Spreading and Retarding Forces

of mass requires that

$$V = Ah \qquad (60)$$

where

A = areal extent of the slick, cm^2

h = mean thickness of slick, cm

The forces which cause oil slicks to spread and/or shrink are identified and considered next.

Surface Tension--

Surface tension forces at the leading edges of oil slicks influence the spreading rate of oils on calm water. Figure 13 shows the direction of surface tension forces acting on a slick. The net value of the balance of the surface tension forces, at any time, determines the contribution of surface tension to the overall spreading rate of the oil. The resultant surface tension (σ) is

$$\sigma = \sigma_w - \sigma_o \cdot \cos \theta_1 - \sigma_{ow} \cdot \cos \sigma_2 \qquad (61)$$

where

$\sigma_w, \sigma_o, \sigma_{ow}$ = surface tensions of water, oil and interfacial tension between oil and water, dynes/cm, respectively

θ_1, θ_2 = instantaneous contact angles formed by the oil phase at the air and water boundaries, degrees, respectively

Oil slick thickness is smallest along the periphery of slicks; the effect of surface tension is significant here because the contact angles are nearly zero. Actually, the contact angles decrease with time as the oil spreads outwards. Since the value of cos θ approaches 1 as θ approaches zero degrees, Equation (61) can be written as

$$\sigma = \sigma_w - \sigma_o - \sigma_{ow} \tag{62}$$

Depending on the value of σ, surface tension forces may accelerate or retard spreading.

A positive value for σ speeds spreading, while a negative value has the opposite effect. The net surface tension divided by the area of the slick gives the surface tension force per unit volume of oil (F_σ)

$$F_\sigma = k_1 \sigma / A \tag{63}$$

where

σ = net surface tension, dynes/cm

A = area of the slick, cm^2

k_1 = proportionality factor

The factor k_1 was introduced to account for the variations of the contact angles and the surface and interfacial tensions with time.

The spreading force due to surface tension may not be uniform along the free surfaces of the oil slick. Variation of surface tension along the periphery of oil slicks are partially responsible for unsymmetric spreading patterns.

Gravity--

The effect of gravity on an oil slick can be evaluated by considering the two components of the gravity vector, g_x (in the direction of spreading) and g_y (normal to the spreading), as

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shown in Figure 13. The component g_y of the gravity force acts vertically downward and produces only hydrostatic pressure. This pressure increases with distance measured downward from the free surface of the oil slick. Since the oil slick is in hydrostatic equilibrium, a hydrostatic balance on the oil is

$$\frac{dP}{dy} = -g_y \rho_o \tag{64}$$

where

P = the hydrostatic pressure on the oil, gm/cm•sec^2

g_y = vertical component of acceleration due to gravity, cm/sec^2

ρ_o = density of oil, gm/cm^3

y = vertical coordinate axis, cm

Integrating Equation (64) over the thickness of the oil layer above the water surface yields the magnitude of the hydrostatic pressure difference (ΔP).

$$P = g_y \rho_o \Delta h = k_2 g \rho_o \Delta h \tag{65}$$

where

k_2 = constant of proportionality

Δh = thickness of the oil layer above the mean water surface, cm

To eliminate Δh from Equation (65), a buoyancy equation is used. Since the oil floats on water, the equation of buoyancy is

$$g \rho_w (h - \Delta h) = g \rho_o h \tag{66}$$

where

Δh = thickness of the oil above mean water level, cm

h = mean oil slick thickness, cm

ρ_w, ρ_o = densities of water and oil, gm/cm^3, respectively

g = gravitational acceleration, cm/sec^2

Solving for Δh gives

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$$\Delta h = (1 - \frac{\rho_o}{\rho_w})h \tag{67}$$

Substituting Equation (67) in Equation (65) yields

$$P = k_2 g \rho_o (1-\rho_o/\rho_w)h \tag{68}$$

The gravity force per unit volume of oil which corresponds to the pressure force is

$$F_g = k_2 g \rho_o (1-\rho_o/\rho_w)\frac{h^2}{A} \tag{69}$$

Eliminating h in Equation (69), using Equation (60), gives

$$F_g = k_2 g \rho_o (1-\rho_o/\rho_w)\frac{V^2}{A^3} \tag{70}$$

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This pressure force is caused by the downward-acting force of gravity, tending to decrease the height of the oil.

The component g_x of the acceleration due to gravity generates flow in the x-direction, also. The magnitude of this force is

$$F_{g_x} = g_x \rho_o h(x) \delta x \tag{71}$$

where

g_x = the x-direction component of the acceleration due to gravity, cm/sec^2

$h(x)$ = variation of oil slick thickness along the x-direction, cm

δx = unit width along the x-axis, cm

Since g_x is much smaller than g_y the influence of F_{g_x} on the spreading oil is negligible.

Viscous--

At the water surface, the dynamics of the spreading process depends on the magnitude of the viscous forces at the air and water interfaces. The air at the top and the water layer in close proximity to the oil, i.e. the water-boundary layer, exert viscous drags on the oil. In the absence of turbulent wind, the

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viscous drag at the air interface is insignificant. The shear stress acting on the oil slick at the oil/water interface is the viscous force which impedes oil spreading. The magnitude of this viscous force per unit volume of oil, F_v, is

$$F_v = \tau A/V \tag{72}$$

where

τ = shear stress exerted by the water column on the oil slick, $gm/cm \cdot sec^2$

For Newtonian fluids, there is a linear relation between shear stress and strain rate or gradient in velocity

$$\tau = \mu_o \frac{dv}{dh} \tag{73}$$

where

μ_o = viscosity of oil, gm/cm·sec

$\frac{dv}{dh}$ = velocity gradient in the oil in the direction of oil thickness, sec^{-1}

If the velocity profile in the oil is assumed to be linear in the vertical direction, then

$$\frac{dv}{dh} \approx \frac{v}{h} = k_3 \frac{v}{h} \tag{74}$$

and

$$v = \frac{\ell}{t} \tag{75}$$

where

k_3 = proportionality constant

v = spreading velocity, cm/sec

ℓ = characteristic length in the direction of spreading ($A = \ell^2$), cm

t = time of spreading, sec

h = mean oil slick thickness, cm

Equation (74) is substituted into (73) to give

$$\tau = \frac{k_3 \mu_o A^{1/2}}{th} \qquad (76)$$

Substituting Equation (76) into (72) yields

$$F_v = \frac{k_3 \mu_o A^{1/2}}{th} \cdot \frac{A}{V} \qquad (77)$$

When h is eliminated in Equation (77) by using Equation (60), the viscous force becomes

$$F_v = \frac{k_3 \mu_o A^{5/2}}{V^2 t} \qquad (78)$$

Inertia--

During the early stages, i.e. the initiation of spreading, the force of inertia is important. As a slick accelerates from rest, the motion is retarded by force of inertia. The magnitude of this force, F_i, can be approximately determined by a momentum balance in the direction of motion of the slick

$$F_i = k_4 \rho_o a \qquad (79)$$

where

ρ_o = mass density of the oil, gm/cm^3

a = acceleration of the oil, cm/sec^2

k_4 = proportionality constant

The acceleration of the oil can be written as

$$a = \frac{\ell}{t^2} \qquad (80)$$

where

ℓ = characteristic length of the oil slick, equals $(A)^{1/2}$, cm

t = time of spreading, sec

The inertia force becomes

$$F_i = k_4 \rho_o A^{1/2}/t^2 \tag{81}$$

Equations of Spreading

The equation of spreading is derived by equating the forces which cause and oppose spreading. These equations are (63), (70), (78), and (81). Thus, the spreading equation is

$$F_\sigma + F_g = F_v + F_i \tag{82}$$

$$k_1 \frac{\sigma}{A} + k_2 g \rho_o (1-\Delta\rho) \frac{V^2}{A^3} = \frac{k_3 \mu_o A^{5/2}}{V^2 t} + \frac{k_4 \rho_o A^{1/2}}{t^2} \tag{83}$$

where

$\Delta\rho = \rho_o/\rho_w$, ratio of oil to water densities

Algebraic manipulation of Equation (83) to solve for A as a function of the other terms is not practical. Following the method of Fay (1969,1971), each of the spreading forces can be equated to the retarding forces and the expression is solved for A to give several spreading regimes.

For $F_\sigma = F_v$ (surface-tension/viscous spreading)

$$k_1 \frac{\sigma}{A} = \frac{k_3 \mu_o A^{5/2}}{V^2 t} \tag{84}$$

$$A = k_5 \left| \frac{\sigma V^2 t}{\mu_o} \right|^{2/7} \tag{85}$$

where $k_5 = (\frac{k_1}{k_3})^{2/7}$.

For $F_\sigma = F_i$ (surface-tension/inertia spreading)

$$k_1 \frac{\sigma}{A} = \frac{k_4 \rho_o A^{1/2}}{t^2} \tag{86}$$

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$$A = k_6 \left| \frac{\sigma t^2}{\rho_o} \right|^{2/3} \qquad (87)$$

where $k_6 = (\frac{k_1}{k_4})^{2/3}$.

For $F_g = F_v$ (gravity/viscous spreading)

$$k_2 g \rho_o (1-\Delta\rho) \frac{V^2}{V^3} = \frac{k_3 \mu_o A^{5/2}}{V^2 t} \qquad (88)$$

$$A = k_7 \left| \frac{g \rho_o (1-\Delta\rho) V^4 t}{\mu_o} \right|^{2/11} \qquad (89)$$

where $k_7 = (\frac{k_2}{k_3})^{2/11}$.

For $F_g = F_i$ (gravity/inertia spreading)

$$k_2 g \rho_o (1-\Delta\rho) \frac{V^2}{A^3} = \frac{k_4 \rho_o A^{1/2}}{t^2} \qquad (90)$$

$$A = k_8 \left| g (1-\Delta\rho) V^2 t^2 \right|^{2/7} \qquad (91)$$

where $k_8 = (\frac{k_2}{k_4})^{2/7}$.

Equations (85), (87), (89) and (91) are functions of only the physical properties of oil and water, volume of oil and elapsed time. These equations relate the areal extent of oil slicks spreading on calm water to elapsed time. It is interesting to find that the equation for the surface-tension/inertia stage is independent of the volume of oil spilled. As such, this equation is not expected to be a good predictor of the area of a slick. The volume of oil spilled is related to the duration of the spill and the time of spreading via Equations (58) and (59).

MECHANISMS OF CHEMICAL DISPERSION OF OIL SLICKS

The importance of dealing with oil spills by diversion, containment and collection of floating oil cannot be underemphasized. These methods are not practical in all spill situations, for several reasons cited earlier. For example, there is a sea-state threshold beyond which containment and recovery of oil slicks are impossible. Dispersion of oil slicks by chemical treatment may be the only option available to reduce adverse impacts on the environment. The economics of this oil spill cleanup method are favorable when aerial spraying can be used and when mixing energy can be provided by winds, waves, tides and currents.

Previous investigations of chemical dispersion of oil slicks were limited to laboratory tests of the effectiveness of dispersants and toxicity to marine life forms. Thus, no phenomenological theories are available to explain the mechanisms of dispersant action on oil slicks during cleanup operations.

In this section, the mass transfer processes that lead to dispersion of oil slicks in water are identified. Primary mechanistic steps are distinguished from those that are ancillary. Mathematical equations are presented to quantify the key mechanisms. The effect of introducing mixing energy into oil/water dispersant systems by using mechanical devices or the action of turbulence generated during high sea states will be discussed in qualitative terms. The limitations of the model will be apparent as consequences of the assumptions made as the model is developed.

Mechanistic Steps

The mechanisms of chemical dispersion are poorly understood. An attempt to explain dispersion of oil slicks with chemical agents was made by Canevari (1969a,b). He proposed three mechanistic steps:

a) diffusion of dispersant molecules through the oil layer;
b) incorporation of oil globules into micelles; and
c) diffusion of micelles into the underlying column of water where they become stranded.

Although these mechanisms are useful in providing a general description of dispersion processes, they do not include all the mass transfer processes that contribute to chemical dispersion. Also, it may be that none of the mechanisms cited is the rate-determining step. Canevari (1969b) described the mode of action of the self-mix dispersants by an analogy to the "diffusion and stranding" mechanism that occurs in spontaneous emulsification processes (Davies and Rideal, 1963).

Chan et al. (1976) used detergency theory to explain the mechanism of solubilization in a detergent-saturated solution. Similarly, Prudich and Henry (1978) discussed their experimental data for the transfer of hydrophilic-coated-mineral-matter particles from a hydrocarbon phase to an aqueous phase using concepts of partial detergency. Drawing from the efforts of these investigators, concepts in colloid chemistry and homogeneous catalysis, an attempt will be made to create a general description of oil slick dispersion using chemical dispersants.

Dispersion practice varies and depends on several factors, e.g. size of oil slick, accessibility of the oil spill site, etc. The case considered here is as follows. Dispersant is applied aerially in a fine mist, such that the droplets settle gently on the oil layer. The impact velocity of the spray is negligible and the dispersant does not penetrate the oil; it forms a uniform film at the surface of the oil slick.

In the absence of body forces in the water column (i.e., prior to mixing of the dispersant/oil/water system) and with sufficient contact between dispersant and oil, the processes that cause transfer of oily material from the oil layer to the aqueous phase are:

a) diffusion of dispersant molecules (and micelles) from dispersant solution to dispersant/oil (d/o) interfaces;
b) distribution of molecules at d/o interfaces;
c) saturation of d/o interfaces;
d) diffusion of molecules through the oil layer to oil/water (o/w) interfaces;
e) distribution of molecules at o/w interfaces;
f) adsorption of micelles at o/w interfaces;
g) formation of mixed micelles and interfacial complexes at o/w interfaces;
h) desorption of mixed micelles from o/w interfaces;
i) diffusion of mixed micelles into the bulk aqueous phase;
j) dissolution/accommodation/solubilization of oil particles in aqueous phase; and
k) diffusion of free molecules back to o/w interfaces or away from the zone of contamination.

These mechanisms give a comprehensive picture of chemical dispersion processes. The fundamental dispersion processes are (f), (g), (h), (i) and (j); these steps are important for anionic, cationic and nonionic dispersants. The other steps are auxilliary. Steps (a) to (e) can be lumped together and considered as a diffusional step across the oil layer. Figure 14 shows the mass transfer processes that are important in dispersion processes.

The relative importance of each of these steps varies, depending on the situation. In some situations, some of the secondary processes can become important. The importance of individual steps or processes depends on the structure of the surface-active agent, the oil, the solvent base used to formulate the dispersant, and the concentration and dosage of the surfactant. For instance, hydrocarbons are generally miscible with

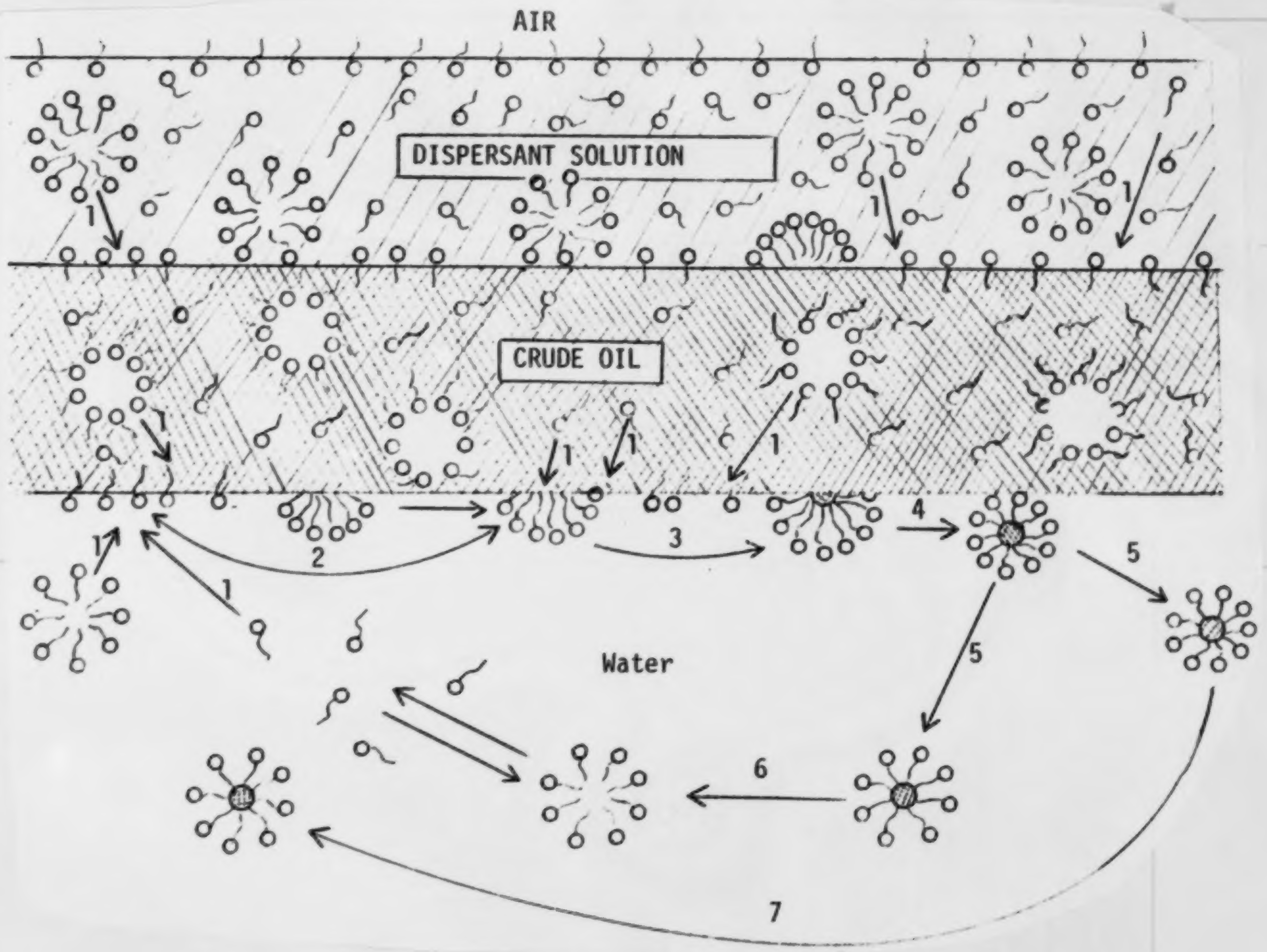

Figure 14. Some Mass Transfer Processes during Chemical Dispersion of Oil Slicks: 1. diffusion of single dispersant molecules or micelles to interfaces; 2. adsorption of molecules at interfaces; 3. formation of mixed micelles and interfacial complexes; 4. desorption of mixed micelles; 5. diffusion of mixed micelles; 6. dissolution of oil in water; 7. accommodation/solubilization of mixed micelles in bulk of liquid.

other hydrocarbons, because of the near zero Gibbs free energy of mixing. Thus, dispersants formulated in hydrocarbon solvents will diffuse through oil slicks faster than those that are aqueous-based.

Formulation of Model Equations

Before mathematical equations are derived for the fundamental processes, a brief discussion of micellization is necessary to an understanding of chemical dispersion of oil slicks.

The behavior of a surface-active agent depends on its state of solution. Generally, dispersion processes are favored if the surfactant is present in the solvent solution as micelles rather than as single ions or molecules. When sufficiently concentrated, dispersant solutions contain micelles. These aggregates are considered to be thermodynamically stable and contain from 10 to more than 100 surfactant molecules. For example, sodium lauryl sulfate ($CH_3(CH_2)_{11}$-$NaSO_4$) forms micelles consisting of 62 molecules (Elworthy et al., 1968).

The size of a micelle is determined by the structure; micelle diameters range from 40 to 100 Å. The concentration of surfactant at which micelles become significant, i.e. the critical micelle concentration (CMC), is related to the number of carbon atoms in a straight chain dispersant molecule by

$$\log CMC = a - bm \tag{92}$$

where

m = the number of carbon atoms

a,b = constants

Nonionic surfactants form micelles at lower concentrations than ionic types, at the same hydrocarbon chain length. Since commercially available dispersant formulations may consist of more than one type of surfactant molecules, the CMC of a mixture will lie between the values of the components.

The law of mass action is usually applied to the association of single molecules to form aggregates and complex molecules. A basic assumption is that equilibrium exists between single molecules and micellar aggregates. For non-ionic surfactants, the reversible process is

$$mC_i \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C_m \tag{93}$$

If the activities are equated to concentrations, the equilibrium constant, K_n, for the micellization of non-ionic dispersants is

$$K_n = \frac{k_f}{k_r} = \frac{C_m}{C_i^m} \tag{94}$$

where

k_f, k_r = rate constants for the forward and reverse reactions, sec^{-1}, respectively

C_m = mass concentration of aggregates or micelles, gm/cm^3

C_i = mass concentration of single surfactant molecules, gm/cm^3

m = the association number for the surfactant

For ionic surfactants, the reversible process is

$$mC_i+(m-p)C_c \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C_m \tag{95}$$

and

$$K_i = \frac{k_f}{k_r} = \frac{C_m}{C_i^m C_c^{(m-p)}} \tag{96}$$

where

C_c = mass concentration of counter-ions, gm/cm^3

p = number of counter-ions not attached to the micelle

The degree of ionization of the ionic surfactant is p divided by m.

If the structure of a dispersant is known, it is possible to determine m. For dispersants with a linear hydrocarbon compound, m equals the number of $-CH_2-$ groups. Unfortunately, information on the structure and types of surface active agents in commercial dispersant formulations is proprietary, and m is unknown for commercial dispersants.

Since micelles in solutions of ionic surface-active agents are charged, they repel each other. According to Hartley (1976), the distance between charged micelles is

$$d^3 = \frac{8\pi}{3\sqrt{2}} \phi r^3 \quad (97)$$

where

d = distance between the centers of the micelles, A°

ϕ = weight fraction of the total volume occupied by micelles

r = micelle radius (assumed spherical), A°

The formation of micelles in dispersant solutions influences the rate of chemical dispersion. The diffusion of surface-active materials to various interfaces and transport of oil droplets into bulk aqueous phase are affected by the degree of micellization. The total quantity of surfactant available for dispersion is increased when surface-active agents are present in crude oils, petroleum products and surface layers of seawater prior to the application of dispersants to oil slicks.

Diffusion of Micelles to Interfaces--

Micelles must diffuse through the dispersant solution and the oil layer to reach oil/water interfaces. A high concentration of surface-active material in the dispersant solution is favorable to high diffusive flux. Dispersants formulated in hydrocarbon solvents approach molecular solution and diffuse rapidly through the oil layer. Dispersants formulated in water must undergo two diffusion steps; through both aqueous solvent and oil layers. Because of these two diffusion steps, the former dispersants may be slightly more efficient than those of the latter type.

Since micelles and unaggregated molecules are in equilibrium in dispersant solutions, both species diffuse but the flux of micelles will be less than for single molecules. The rate of a diffusion process may be expressed by Fick's First Law. For simple diffusion, Fick's Law can be written for micelles and single molecules.

$$F_m = -D_m \frac{\partial C_m}{\partial x} \quad (98)$$

$$F_i = -D_i \frac{\partial C_i}{\partial x} \quad (99)$$

where

F_m, F_i = mass fluxes of micelles and single molecules, gm/cm^2·sec, respectively

D_m, D_i = diffusion coefficients of micelles and dispersant molecules, cm^2/sec, respectively

$\frac{\partial C_m}{\partial x}, \frac{\partial C_i}{\partial x}$ = local concentration gradients in the direction of diffusion, gm/cm^4

The combined diffusive flux (F_d) for both species is

$$F_d = F_m + F_i \tag{100}$$

The actual F_d will be smaller than the sum of the individual fluxes because of interactions between the diffusing species and the effect of other intermolecular forces.

Diffusion coefficients of micelles and single molecules can be estimated from the simple Stokes-Einstein Equation

$$\overline{D} = \frac{N_B T}{6\pi\mu r} \tag{101}$$

where

$\overline{D}$ = diffusion coefficient, cm^2/sec

N_B = Boltzmann's constant, dynes cm/°K

T = absolute temperature, °K

μ = viscosity of solvent, dynes·sec/cm^2

r = mean hydrodynamic radius of the micelle or molecule, cm

The diffusion coefficient for single molecules will be greater than that for a micelle.

Ward and Tordai (1946) derived an expression for the rate of diffusion of molecules to interfaces. They applied the penetration theory of mass transfer across a liquid-liquid interface and derived the following equation for the rate of diffusion

$$\frac{dn}{dt} = \left(\frac{D}{\pi t}\right)^{1/2} \cdot \left(\frac{N_A}{1000}\right) \cdot C \tag{102}$$

where

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n = the number of molecules arriving at a unit cross sectional area of the interface, molecules/cm^2

D = diffusion coefficient of the molecule through the medium, cm^2/sec

t = time, sec

N_A = Avogadro's number, 6×10^{23} molecules/gm-moles

C = concentration of surface-active molecules diffusing from the surface, gm-moles/ℓ

Equation (102) assumes

a) molecules diffuse at a uniform velocity;
b) there is no back-diffusion; and
c) there is no energy barrier, mechanical mixing or thermal convention in the medium

When an energy barrier opposes the process, a lower rate of diffusion will result. This equation is applicable to the diffusion of single molecules, micelles, and mixed micelles.

Equation (102) can be integrated to give

$$n = 2\left(\frac{Dt}{\pi}\right)^{1/2}\left(\frac{N_A}{1000}\right)\cdot C \qquad (103)$$

The diffusion of surface-active agents from the bulk oil layer to o/w interfaces will be rapid because it involves molecular diffusion and small oil slick thicknesses.

At the interface, micelles dissociate into single molecules prior to adsorption and when sufficient molecules have been adsorbed, some molecules "react" with oil particles to form mixed micelles that desorb. The proposed reaction between m molecules and oil to form a mixed micelle is

$$mC_i + O \rightleftharpoons C_mO$$

The assumed sequence of reversible steps is

(1) $$C_i + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_iS) \qquad \text{(Adsorption)}$$

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(2) $$m(C_iS)+O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (C_mOS_m) \quad \text{(Reaction)}$$

(3) $$(C_mOS_m) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_mO+mS \quad \text{(Desorption)}$$

where

C_i = concentration of single molecules

C_mO = concentration of mixed micelles

S = an adsorption site

m = number of adsorption sites

(C_iS) = adsorbed single molecule

(C_mOS_m) = adsorbed mixed micelles

O = concentration of oil

The individual steps are next considered in greater detail.

Adsorption of Dispersant Molecules--

The rate of adsorption of surface-active molecules at o/w interfaces is governed by the rate of diffusion from the oil layer. Since single molecules and micelles diffuse together, they arrive jointly at o/w interfaces where they adsorb as single molecules.

From step 1, the rate of adsorption is

$$r_1 = k_1C_iS-k_{-1}(C_iS) \tag{104}$$

where

C_i = concentration of surfactant molecules

S = an adsorption site

(C_iS) = concentration of adsorbed molecules

k_1,k_{-1} = adsorption coefficients for the forward and reverse reactions

All concentration terms refer to concentrations at the interface. The adsorption coefficients follow Arrhenius' Law

$$k = k_0 \exp(-E/RT) \tag{105}$$

where

k_0 = frequency of adsorption, sec^{-1}

E = energy of adsorption, cal/gm-mole

R = gas constant, cal/gm-mole·K

T = absolute temperature, K

At equilibrium, the rates of the forward and reverse reactions are equal

$$Sk_1C_i = k_{-1}(C_iS) \tag{106}$$

and

$$K_1 = \frac{k_1}{k_{-1}} = \frac{(C_iS)}{SC_i} \tag{107}$$

where K_1 is the equilibrium adsorption constant.

Surfactant molecules are held at the interface by molecular forces. They are oriented with hydrophobic groups anchored to the oil phase and hydrophilic groups immersed in the aqueous phase.

Formation of Mixed Micelles and Interfacial Complexes--

When a sufficient number of dispersant molecules have been adsorbed at the interface, a "reaction" occurs between a number "m" of absorbed molecules which are close neighbors and micro oil particles to form mixed micelles and/or interfacial complexes. The stoichiometry of this "reaction" is not known. The reaction may be a simple coexistence of oil and dispersant molecules as the oil particles are merely incorporated into the hydrophobic core of the micelles. The formation of mixed micelles is an important mechanism in the chemical dispersion of oil. If the reaction is assumed to be bimolecular, then the rate of the reaction can be written as

$$r_2 = k_2O(C_iS)^m - k_{-2}(C_mOS_m) \tag{108}$$

where

O = amount of oil particle incorporated into the micellar core

(C_mOS_m) = surface concentration of adsorbed mixed micelles

k_2, k_{-2} = coefficients of the forward and reverse reactions

Free oil is always in excess at the interface and Equation (108) can be simplified to

$$r_2 = k_2'(C_iS)^m - k_{-2}(C_mOS_m) \tag{109}$$

where $k_2' = k_2O$

The equilibrium constant for the reaction is

$$K_2 = \frac{k_2'}{k_{-2}} = \frac{(C_mOS_m)}{(C_iS)^m} \tag{110}$$

This reaction will not occur if the number of molecules adsorbed on adjacent sites is less than the association number of the surface-active compound.

Desorption of Mixed Micelles--

The desorption of mixed micelles from the interface exposes additional surfaces for adsorption of molecules arriving at the interface by diffusion from the oil layer. In this process, m adsorption sites become available. The rate of desorption according to step 3 is

$$r_3 = k_3(C_mOS_m) - k_{-3}S^mC_mO \tag{111}$$

where

(C_mOS_m) = concentration of adsorbed mixed micelles

C_mO = concentration of mixed micelles at the interface

S^m = "m" number of adsorption sites which is equal to mS

k_3, k_{-3} = desorption coefficients

At equilibrium, the desorption constant K_3 is

$$K_3 = \frac{k_3}{k_{-3}} = \frac{S^mC_mO}{(C_mOS_m)} \tag{112}$$

As the mixed micelles desorb from the interface, they take with them oil particles that are occluded in their core regions.

The coefficients of the reaction and desorption steps follow Arrhenius' Law, also. Davies and Rideal (1963) present equations for estimating the desorption energies (E) of some nonionic and ionic surfactants for a few interfaces in which the bottom phase is water. For nonionic and ionic surfactants, the equations are

$$E = \lambda_p + mw \tag{113}$$

and

$$E = \lambda_p + mw - z_1 \varepsilon \psi_o \tag{114}$$

where

λ_p = energy of polarization of the unionized polar group, cal/g-mole

m = the number of $-CH_2-$ groups

w = van der Waals adsorption energy associated with each $-CH_2-$ group, cal/gm-mole

z_1 = valency of the surface-active ion

ε = electron charge

ψ_o = electrical potential of the surface

Comparison of Equations (113) and (114) shows that the desorption energies of nonionic surfactants are usually greater than those of ionic agents of the same chain length. Davies and Rideal (1963) give values for 1mM of sodium laurly sulfate for a paraffinic oil/water interface, with no salt added, as

$$\lambda p = +160 \ (20C), \ +1800 \ (50C)$$

$$w = +810$$

$$z_1 \varepsilon \psi_o = -5000$$

In the presence of salt, the value of $z_1 \varepsilon \psi_o$ increases.

Diffusion of Mixed Micelles into the Aqueous Phase--

As mixed micelles desorb from the interfaces, the layer directly below the interface becomes saturated with mixed micelles. The concentration gradient that builds up between this layer and the bulk aqueous phase provides the driving force that causes mixed micelles to diffuse away from the surface layer. This diffusion step is similar to the diffusion of single dispersant molecules and micelles. Equation (102) is applicable to this mass transfer.

Dissolution/Accommodation/Solubilization of Oil in the Aqueous Phase--

The transfer of oil into the underlying column of water is the ultimate goal of chemical dispersion. During the initial stages of the dispersion process, the concentration of oil in the aqueous phase is nearly zero. Then, as the mixed micelles diffuse into water, dissolution of the oil in water occurs. The first micelles release their oil particles into water, where the oil goes into molecular solution. The mixed micelles become unaggregate molecules and, if the oil/water system is static, these molecules diffuse back to the interface. In this case, there is no net loss of dispersant; but, in flow systems, the dispersant molecules may be flushed away from the zone of contamination.

As the diffusion of mixed micelles into the water layer continues, the concentration of oil increases. In time, oil in water will be present as molecularly dissolved, accommodated and solubilized species. These forms coexist in water until the system reaches "supersaturation." At this point, microemulsions are formed. These coalesce into larger particles that can become buoyant, rise and recoalesce with the surface slick. These processes occur only in chemically treated and static oil/water systems when the dosage of dispersant is large enough to lead to accommodation/solubilization/microemulsion phenomena. Except in heavily contaminated waters, these phenomena will not take place in flow systems as dilution of oil in solution occurs continuously by inflowing fresh water.

The combined rate of these processes is derived from a material balance on the oil in solution. The rate of change of oil concentration in the aqueous phase is equal to the rate of molecular diffusion of mixed micelles from the interface which is assumed to be saturated. It follows that

$$R = K_L(C_mO-\overline{C}) \qquad (115)$$

where

K_L = overall liquid mass transfer coefficient

C_mO = concentration of mixed micelles at the o/w interfaces on the water side

$\overline{C}$ = average concentration of oil in the aqueous phase

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The concentration of oil in water consists of oily material from the slick as well as hydrophobic portions of mixed micelles in solution. Under field conditions, some oil may sediment after adsorbing onto solid particles in suspension.

The Rate-Determining Step

The concept of a rate-limiting step is useful when considering a sequence of several steps. If a step is assumed to be the slowest step, then its rate controls the rate of the overall reaction. All steps except the limiting step are assumed to be at steady-state or in equilibrium and the overall rate is derived in terms of the slowest step and relevant parameters.

The diffusion steps are probably not rate-limiting as some mixing is usually available to chemically treated oil/water systems. The effect of mixing on oil/water/dispersant systems will be discussed later. Thus, the rate-determining steps are most likely adsorption, reaction or desorption.

Adsorption Control Model--

Adsorption is a surface phenomenon and is important in homogeneous and heterogeneous catalysis. Several models have been proposed in the literature for the kinetics of adsorption. The model used here is based on the treatment by Langmuir-Hinshelwood-Hougen-Watson (Carberry, 1976). This treatment assumes i) monolayer coverage, ii) no interactions between adsorbed molecules, and iii) homogeneous surfaces and uniformly energetic adsorption sites. By mass-action, the rate of adsorption is proportional to the concentration of the adsorbent and the fraction of the surface that is unoccupied (θ)

$$r_A = k_1 C_i (1-\theta) \qquad (116)$$

where k_1 is the adsorption coefficient.

The total concentration of adsorption sites includes those either vacant or containing adsorbed species. It follows that

$$S_o = S+(C_iS)+(C_mOS_m) \qquad (117)$$

where S_o = total concentration of adsorption sites

S = adsorption sites that are vacant.

The equilibrium constants are used to eliminate the adsorbed species in Equation (117). From Equation (107), (C_iS) is equal to

$$(C_iS) = SK_1C_i \qquad (118)$$

Since all sites are identical and if all surfactant molecules are similar, Equation (118) can be written as

$$(C_iS)^m = mK_iC_iS \tag{119}$$

and

$$mK_1 = \frac{(C_iS)^m}{C_iS} \tag{120}$$

The product of Equations (110) and (118) is solved for (C_mOS_m) to give

$$(C_mOS_m) = mSK_1K_2C_i \tag{121}$$

If Equations (118) and (121) are substituted into (117), the result is

$$S_o = S+SK_1C_i+mSK_1K_2C_i \tag{122}$$

Equation (122) can be written as

$$\frac{S}{S_o} = \frac{1}{(1+K_1C_i+mK_1K_2C_i)} \tag{123}$$

Since Equation (123) is equal to $(1-\theta)$, i.e. the fraction of the interface that is unoccupied, the expression for the adsorption-control model, Equation (116), becomes

$$r_A = \frac{k_1C_i}{(1+K_1C_i+mK_1K_2C_i)} \tag{124}$$

The interfacial concentration term C_i cannot be measured directly. The procedure to relate C_i to C_mO is as follows. First, Equations (110), (112) and (120) are multiplied; the result is

$$mK_1K_2K_3SC_i = S^mC_mO \tag{125}$$

Using the relation $mS = S^m$ and solving for C_i gives

$$C_i = \frac{C_mO}{K_1K_2K_3} \tag{126}$$

Substituting Equation (126) into (124) and simplifying the result shows that

$$r_A = \frac{K_A C_m 0}{(1+K_B C_m 0+K_C C_m 0)} \tag{127}$$

where $K_A = k_1/K_1K_2K_3$

$K_B = 1/K_2K_3$

$K_C = m/K_3$

The interfacial concentration term (C_m0) cannot be measured directly, also; it must be related to the concentration of oil in the bulk water phase through Equation (115).

Interfacial Reaction Control Model--

The rate of reaction is

$$r_R = k_2'(C_iS)^m - k_{-2}(C_m0S_m) \tag{128}$$

Substituting for the adsorbed species using Equations (120) and (121) gives

$$r_R = mk_2'K_1SC_i - mk_{-2}SC_m0/K_3 \tag{129}$$

where S^m has been replaced with mS. Equation (129) is simplified to give

$$r_R = [mk_2'K_1C_i - mk_{-2}C_m0/K_3]S \tag{130}$$

Substituting for S using Equation (123), results in

$$r = \frac{[mk_2K_1C_i - mk_{-2}C_m0/K_3]S_o}{(1+K_1C_i+mK_1K_{eq}C_i)} \tag{131}$$

If, however, C_i is replaced in Equation (131) by using Equation (126), the result simplifies to

$$r = \frac{(k_2'/K_{eq}K_3 - k_{-2}/K_3)mS_oC_m0}{(1+K_BC_m0+K_cC_m0)} \tag{132}$$

where

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$K_B = 1/K_{eq}K_3$

$K_c = m/K_3$

K_{eq} = overall equilibrium constant

$= k_2'/k_{-2}$

Equation (132) is the overall rate of dispersion when the formation of micelles is the controlling step.

Desorption-Control Model--

In Langmurian terms, the rate of desorption is assumed to be proportional to the concentration of the desorbing specie(s) or the fraction of the surface occupied, θ. Thus, the rate of desorption is

$$r_D = k_3(C_mOS_m) = k_3'\theta \tag{133}$$

6-1/2"

Substituting for (C_mOS_m) using Equation (121) gives

$$r_D = mk_3K_1K_2SC_i \tag{134}$$

3-1/8"

If S is replaced in Equation (134) with Equation (123), the result it

$$r_D = \frac{mk_3K_1K_2S_oC_i}{(1+K_1C_i+mK_1K_2C_i)} \tag{135}$$

Substituting for C_i using Equation (126) and simplifying gives

$$r_D = \frac{K_DC_mO}{(1+K_BC_mO+K_CC_mO)} \tag{136}$$

where

$K_D = mk_{-3}S_o$

$K_B = 1/K_2K_3$

$K_C = m/K_3$

This equation is similar to that derived for the case when the rate of adsorption is the limiting step. Also, Equation (136) is related to the concentration of oil in the bulk fluid through Equation (115).

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When mixed micelles desorb from the interface, surfactant molecules are lost from the surface areas. Desorption of mixed micelles exposes additional areas at the interface. Thus, space is available for adsorption of surface-active molecules reaching the interface by diffusion from the bulk oil or water column.

The overall rate of dispersion of chemically treated oil spills will vary according to the mechanism(s) which is(are) rate-limiting. Field conditions will determine the mechanism which is the slowest step.

The Effect of Mixing

Mixing is usually supplied to oil slicks after they are treated by dispersants by mechanical means and/or water motions induced by the action of winds, waves, tides, and currents. The hydrodynamics of the system will vary according to the origin and intensity of mixing.

The amount of work required to remove completely a unit of oil from the oil layer is called the work of detergency. The magnitude of this work for complete detergency is

$$W_d = \sigma_w + \sigma_o - \sigma_{ow} \qquad (137)$$

where

W_d = work of detergency, dynes/cm

$\sigma_w, \sigma_o, \sigma_{ow}$ = surface tensions of water and oil, and interfacial tension between oil and water, dynes/cm, respectively

The presence of surfactants at oil/water interfaces causes reduction in interfacial tension between oil and water and leads to lower values of W_d. Also, a high energy barrier must be overcome for mixed micelles to form and desorb from oil/water interfaces; therefore, the system must be supplied with additional energy for complete detergency. When the work of detergency is equal to or less than the work input into the system, complete dispersion may occur. If the energy input is less than W_d, dispersion will not be complete.

It is important to be able to estimate the amount of mixing energy required to achieve a specific degree of emulsification. Unfortunately, one of the difficulties in effective dispersant treatment of oil spills is the inability to estimate the fraction of energy input available to aid detergency. In the field, the largest part of the energy introduced into the system is dissipated into the water column. Inadequate mixing has adverse effects on chemical dispersion as dispersant can be transported through the water phase before mixed micelles are formed. Therefore, it is not surprising that greater efficiencies are usually reported for small scale laboratory tests of the effectiveness of dispersants, in which the energy input per unit volume of fluid is large. It is necessary to allow the oil and dispersant to make sufficient contact prior to agitating the system.

The rate of input of mechanical energy is important as it influences the total area of oil/water interfaces available for the mass transfer processes discussed earlier. Additional oil/water interfaces are created as the oil layer is physically sheared into droplets according to the following equation

$$A = W_k/\sigma_{ow} \tag{138}$$

where

W_k = amount of energy required to create the interfaces

Stability of the oil droplets is a function of mechanical energy input and other factors. If the intensity of agitation is low, oil droplets that are formed will be coarse and unstable. Unstable phases will tend to remain dispersed only in the presence of turbulence. In the absence of turbulence, or after these phases have migrated to regions of low shear, coalescence is possible; these droplets may coalesce with the parent slick or form separate patches.

Fine oil droplets will form if a system is agitated sufficiently; these droplets are stable and resist coalescence. Weathering processes, turbulent diffusion, waves, currents and tides, and Brownian diffusion transport oil droplets through the water column to points far from the source of the spill. The movement of dispersed oil droplets in water depends on hydrostatic and hydrodynamic forces and the sizes of the droplets.

NUMERICAL ANALYSIS OF DISSOLUTION AND SPREADING EQUATIONS USING EXPERIMENTAL DATA

The dissolution model was tested with experimental data. The values of four parameters in the segmented model are unknown, and must be estimated for any oil. These parameters are C_S, t_m, K_L, and K_E. For each oil tested, a value for the joint point, t_m, was estimated from the experimental data. Since t_m corresponds to the time when oil concentration is maximum, the data in columns 2 (Tables 6 and 7) served as input values for t_m during the regression analysis. Similarly, C_S corresponds to oil concentrations at saturation. The input values for this parameter are listed in Table 8. The initial estimates for K_L and K_E were unity.

The equations of spreading are functions of the volume of oil, the duration of the spill, physical properties of oil and water phases, and time of spreading. In each equation, only the value of one empirical constant must be determined from experimental data. Iteration was started with unity as the initial estimate of the constants in the four spreading equations.

Least-squares regression analysis of the dissolution functions and spreading equations was performed on an IBM 360/370 computer using the SAS (Statistical Analysis System). SAS is a commercial statistical package that is widely used and highly documented (SAS Institute, 1979). Minimum programming effort is required and the package has been tested adequately. The Marquardt method was used to estimate unknown parameters. This method is available as an option in the nonlinear parameter estimation program (NLIN) of the SAS package. NLIN regresses the residuals on the partial derivatives of the functions with respect to the parameters until the iterations converge. The Marquardt procedure is an extension of the Gauss-Newton and Steepest Descent methods and can converge with relatively poor starting guesses for the unknown parameters (Marquardt, 1963). The least squares objective function which is minimized is the sum of the squares of the residuals between the predicted values and experimental data. The built-in convergence criterion in the NLIN program has a value of 10^{-8}.

The listings of sample computer programs, used to run the regression analyses and estimate unknown parameters in the dissolution and spreading models are given in Tables F1 and F2 of Appendix F.

SECTION 9

RESULTS AND DISCUSSION

DISSOLUTION

The rates of dissolution in water of crude oils and processed petroleum have been investigated in open static tests. The tests correspond to the worst condition of an oil spill, e.g. oil completely covering the surface of a small lake. Oils were equilibrated with water at 25C for periods of 2 to 3 weeks and oil concentrations in solution were measured routinely by infrared spectrophotometry.

Tap Water Studies

In studies using tap water as the test fluid, 9 crude oils, 2 processed oils and an oil mixture containing 8% crude and the remaining processed oil were investigated. Experimental data for oil concentrations and equilibration time have been presented in Appendix B.

The results of solubility measurements suggest the old adage "that oil does not mix with water" is false. The concentration profiles for all oils increased gradually during the first few days of equilibrium, reached maximum levels within 9 days and decreased afterwards. Maximum concentration levels were not achieved after equivalent periods of equilibration, but all oil concentrations stabilized after approximately 12 days of equilibration. Despite variations in maximum solubility levels, experimental data for all oils showed similar trends, except Suniland crude which reached maximum solubility in water in the first day. Since samples were taken daily, it is not known whether this crude actually achieved maximum solubility earlier.

The range of oil concentrations varied from zero to a little less than 200 ppm. Generally, the processed oils, i.e., #2 and #6 fuel oils, were less soluble than the crude oils. The rate and extent of solution of an oil depends on the chemical composition of the oil. Crude oils from Brass River and Arzew exhibited similar solubility behavior that differed slightly from the other crude oils. The rates of dissolution of these two crudes were stable for the first few days, then accelerated, until maximum solubility levels were reached. Ironically, these two crudes are from the same geographical area (Algeria). Table 6 shows the maximum concentrations in solution and the time these maximum concentrations were reached.

Salt Water Studies

The rates of dissolution of 5 crude oils and one refinery product were investigated in aqueous solutions containing 3.5% sea salt. The experimental data are presented in Appendix C.

In general, solubility levels in salt solutions are lower than those in tap water. Thus, the rates of dissolution are lower. Longer equilibration periods were also required to achieve maximum concentrations in salt solution. The only exception is Brass River crude. Table 7 shows the maximum concentration levels and required equilibration periods. The last column shows the percent difference when maximum concentrations in tap and salt water are compared. The solubilities of #2 fuel oil in tap and salt water are comparable. Decreases of up to 99% occurred for Alaska and Brass River crudes. These results indicate that hydrocarbon levels in seawater will be much lower than in fresh water systems.

Oil concentration levels in salt water represent the levels that would exist in marine waters with equivalent salt content. The effect of sea salts is to decrease the solubility of oils by "salting-out" hydrocarbons. In marine environments, this reduction in solubility may be offset by the presence of dissolved organic matter in sea water. These materials can solubilize oils and increase the solubilities of oils in salt water beyond the limits of solubilities in tap water.

Saturation Studies

The concentration of oil in water at saturation was determined for each oil. These tests were conducted in closed vessels and the oil/water systems were allowed to equilibrate for 3 months.

Oil concentrations at "saturation" are given in Table 8. For any oil, the concentration at saturation is significantly greater than the maximum solubility in open water (Table 6). It is necessary to caution that these values may not be true saturation concentrations; however, they should be close due to the prolonged equilibration of the oil and water systems in closed vessels.

TABLE 6

Maximum Solubilities of Oils in Tap Water and Times to Attainment

Oil	Time (t_m) (days)	Maximum Solubility (ppm)
Nigerian Crude	6	4.5
Lagunillas Crude	9	2.5
La Rosa Crude	5	3.4
#2 Fuel	7	1.7
#6 Fuel	2	0.9
Suniland Crude	1	61.2
Alaska Crude	3	152.1
8% Crude	2	78.6
Iranian Crude	4	15.0
Sahara Crude	2	24.0
Brass River Crude	8	176.0
Arzew Crude	8	196.0

Comparison of Predictions by the Dissolution Model and Experimental Data

During regression, the values of the parameters in the dissolution equations are adjusted in the iterative process to give final values that best fit the equations to experimental data. Convergence was achieved in all numerical analyses. Table 9 summarizes the final values of the four parameters for all the oils. Statistical tests of the significance of the values of K_L and K_E showed that these parameters are significantly different from zero. The correlation coefficients, R^2, are close to unity, indicating that there is good correlation between the model and experimental data. Correlation coefficients were less than 0.9 in only two cases: Brass River and Arzew crudes.

The final values of the two mass transfer coefficients, K_L and K_E, vary for different oils but all values are smaller than unity. Variations in the final values of the mass transfer coefficients are caused by the different characteristics of the

TABLE 7

Maximum Solubilities of Oils in Salt Water and Times to Attainment

Oil	Time (t_m) (days)	Maximum Solubility (ppm)	Decrease + (%)
Nigerian	14*	1.5	67
La Rosa, Venezuela	12-13	2.5	26
North Slope, Alaska	4	1.1	99
Brass River, Algeria	4	1.4	99
Iranian	7	1.5	90
#2 Fuel	5-6	1.5	12

* End of Equilibration
+ Based on Maximum Solubility in Tap Water

soluble and volatile components in the oils. In tests using tap water, K_E was always larger than K_L; but the reverse is true in tests using salt water. Several factors that were not investigated influence K_E and K_L. They are the temperature of the bulk oil and water phase, salinity, and pH. In the field, K_E and K_L are functions of several other factors, such as the wind velocity profile above the oil layer, turbulence in the water phase, and water quality. The final values of C_s, in six out of twelve oils, converged to the experimental "saturation" concentrations tabulated in Table 8. The differences were small in those cases where the values did not agree. The values of C_s in tests conducted in salt water are smaller than those in tap water and reflect the lower solubilities of oils in salt water. The final values of t_m correspond to the times required for the oils to reach maximum solubility in the specific medium. These values are comparable to those given in Tables 6 and 7.

Comparison of concentration-time profiles, using the dissolution model and experimental data, can be made by considering Figures 15 to 20. Experimental data and model profiles are shown in Figure 15 for #2 and #6 fuel oils, and crudes from Nigeria, Lagunillas and La Rosa. The dissolution model predicts experimental data fairly accurately in all cases. The profiles for Suniland, Sahara and Iranian crudes, and the oil mixture contain-

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TABLE 8

Oil Concentrations at "Saturation"

Oil	Concentration (C_S) (ppm)
Nigerian Crude	29.9
Lagunillas Crude	13.7
La Rosa Crude	17.4
#2 Fuel	9.3
#6 Fuel	21.12
Suniland Crude	102.6
Alaska Crude	235.8
8% Crude	120.9
Iranian Crude	23.3
Sahara Crude	35.6
Brass River Crude	270.7
Arzew Crude	306.0

ing 8% crude are displayed in Figure 16. The results show that the predictions by the model are comparable with experimental data for Sahara and 8% crudes, but the dissolution model does not fit the data as well for crudes from Iran and Suniland. Disparities occur during the later stages of equilibration. Figure 17 compares the results of the model and data for Alaska, Brass River, and Arzew crudes. The fit between the data and the model is good for Alaska crude; it is poor for Brass River and Arzew crudes, because of the significantly different behavior of these two crudes.

Profiles of the dissolution model and experimental data, from solubility studies of #2 fuel oil and Iranian and Brass River crudes in salt water, are displayed in Figure 18. Similar graphs are shown in Figure 19 for Nigerian, Alaskan and La Rosa crudes. The model predicts experimental data accurately in all cases. Figure 20 shows the data and model for Nigerian crude using the results of tests in tap and salt water. Despite slightly different behaviors of the crude,in the two test liquids, the data and models indicate that the final concentrations are similar.

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TABLE 9

Comparison of Final Values of Parameters from Fitting Dissolution Model to Experimental Data

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	Parameters				
Oil	K_L (day^{-1})	K_E (day^{-1})	t_m (day)	C_s (ppm)	R^2
A. Tap Water					
Nigerian Crude	0.055	0.0801	3	29.9	0.993
La Rosa Crude	0.040	0.090	5	17.4	0.989
Lagunillas Crude	0.025	0.080	8	13.7	0.994
#2 Fuel	0.06	0.110	7	5.0	0.980
#6 Fuel	0.012	0.098	4	15.0	0.948
Iranian Crude	0.42	0.300	4	17.0	0.960
Sahara Crude	0.60	0.260	2	35.6	0.990
Suniland Crude	0.90	0.951	1	100.0	0.922
8% Crude	0.71	0.163	1.5	144.6	0.988
Alaska Crude	0.20	0.28	3	290.0	0.968
Brass River Crude	0.07	0.601	9	270.0	0.860
Arzew Crude	0.07	0.540	8	306.0	0.860
B. Salt Water					
#2 Fuel	0.330	0.060	5	2.0	0.992
Iranian Crude	0.220	0.01	6	2.0	0.996
Brass River Crude	0.299	0.025	3.8	2.0	0.997
La Rosa Crude	0.054	0.044	11	6.0	0.980
Alaska Crude	0.060	0.06	3	5.0	0.962
Nigerian Crude	0.120	0.05	12	2.0	0.978

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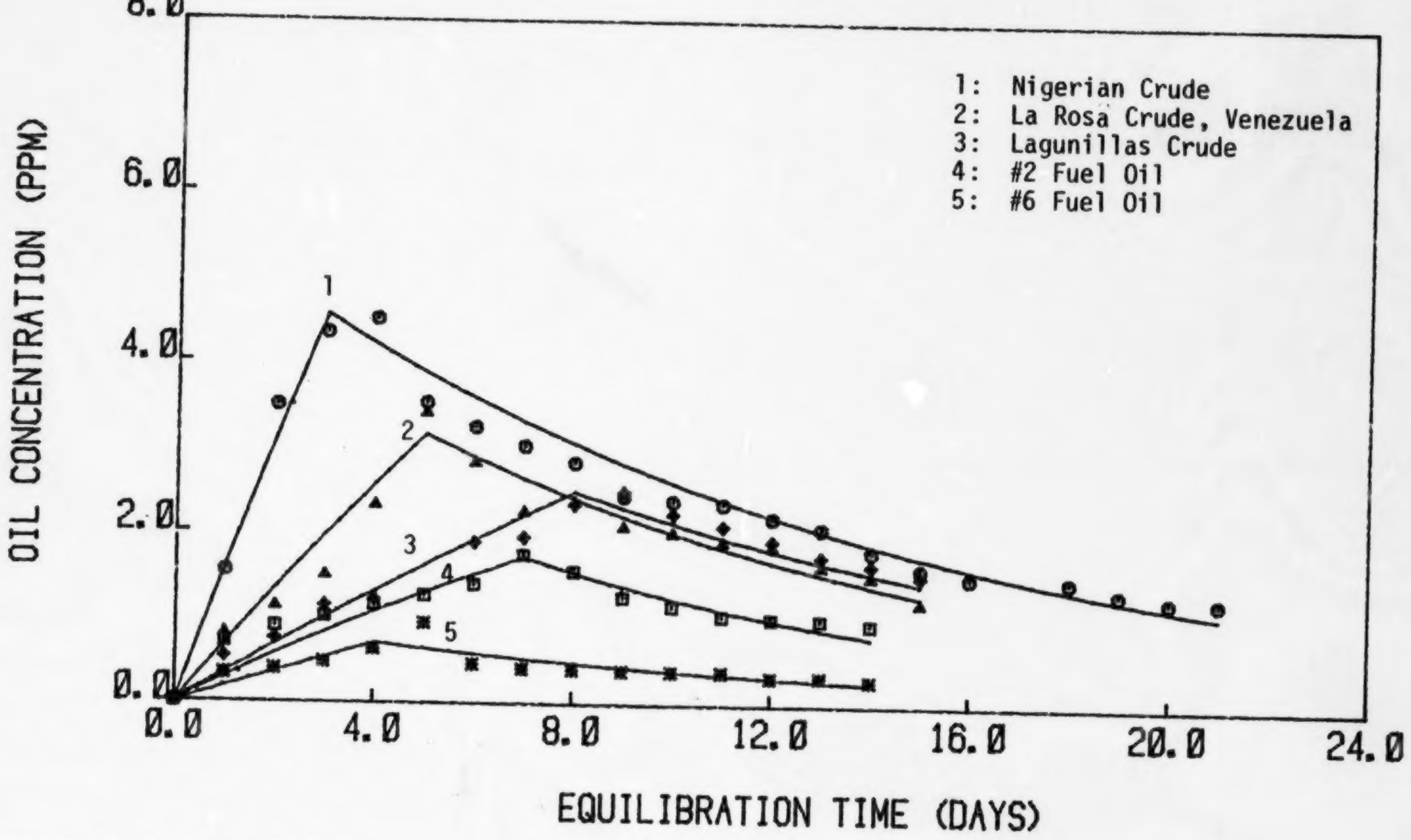

Figure 15. Comparison of Profiles of Dissolution Model and Experimental Data for #2 and #6 Fuel Oils and Crudes from Nigeria, La Rosa (Venezuela) and Lagunillas - Tap Water

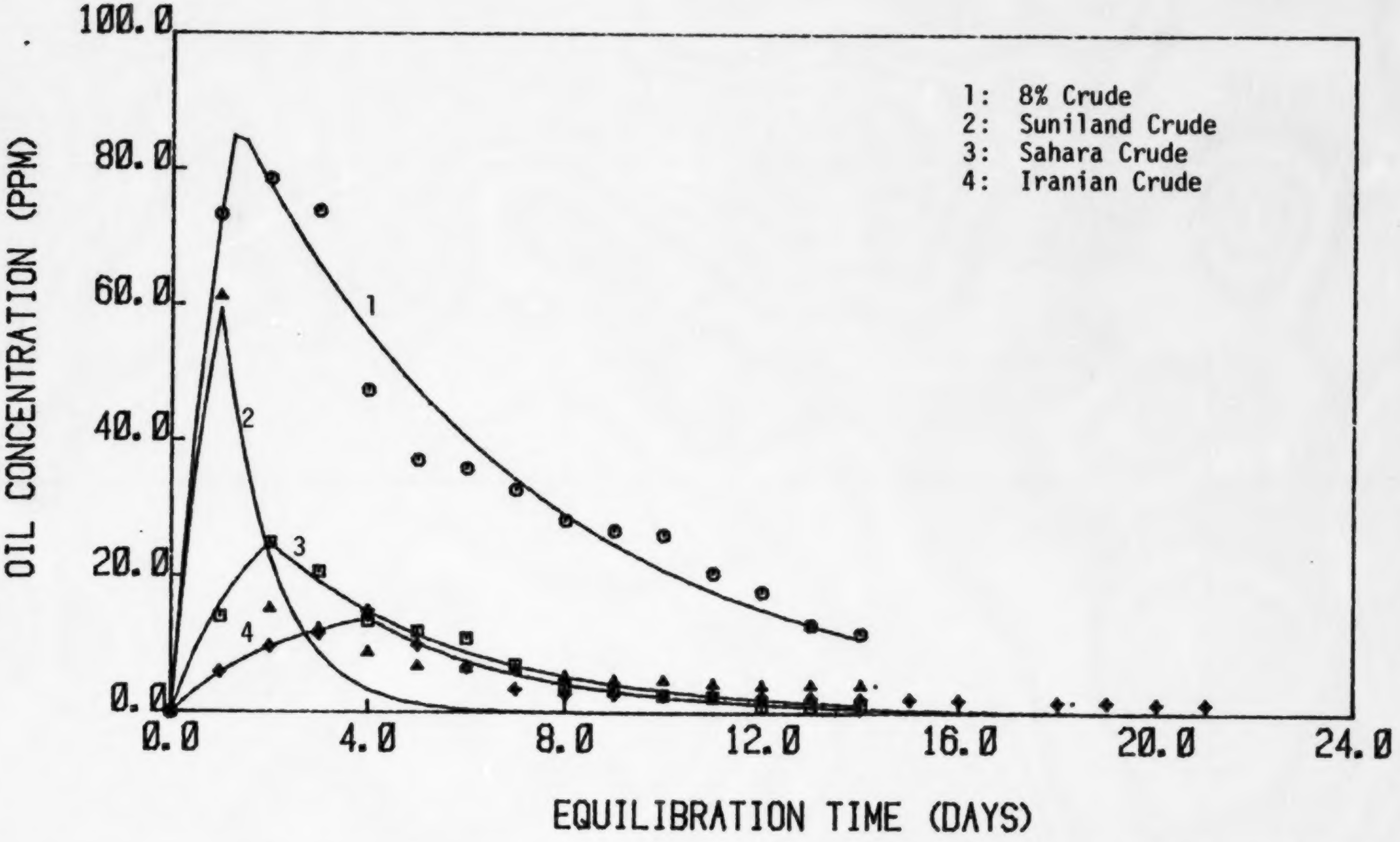

Figure 16. Comparison of Profiles of Dissolution Model and Experimental Data for Crudes from Suniland, Sahara, and Iran, and 8% Mixture of Crude Oil and Processed Oil - Tap Water

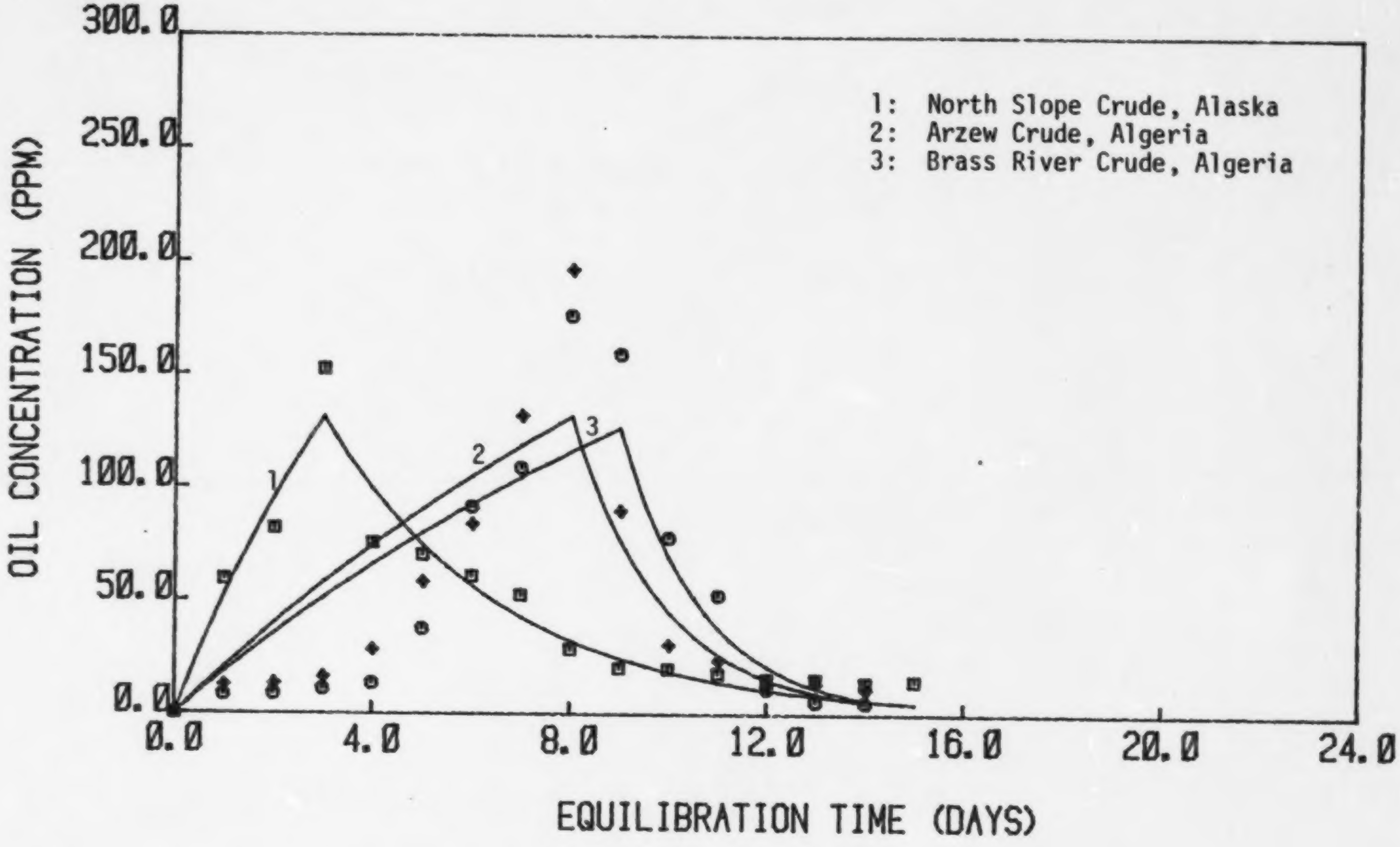

Figure 17. Comparison of Profiles of Dissolution Model and Experimental Data for Crudes from Alaska, Arzew and Brass River (Algeria) - Tap Water

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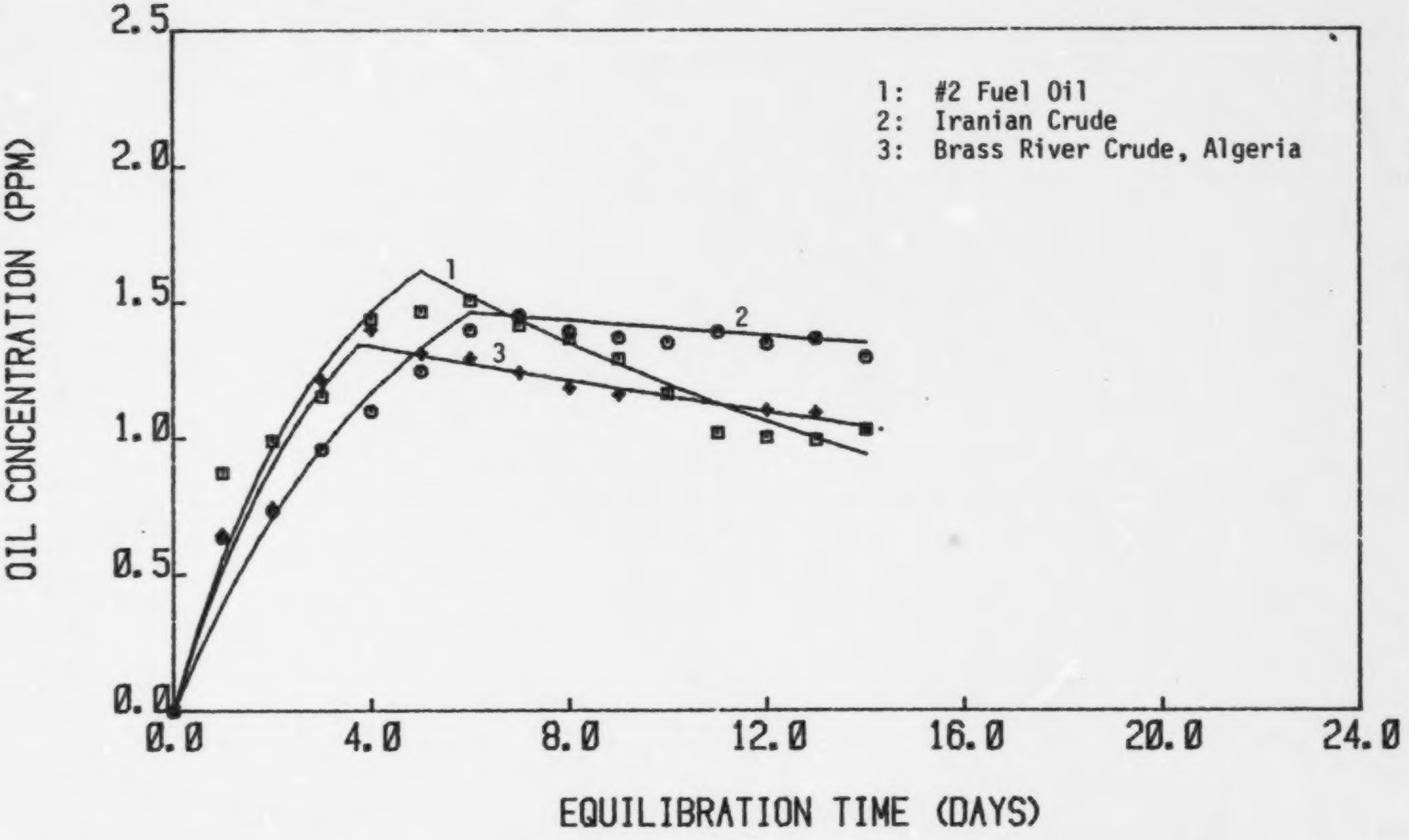

Figure 18. Comparison of Profiles of Dissolution Model and Experimental Data for #2 Fuel Oil, Iranian and Brass River Crudes - Salt Water

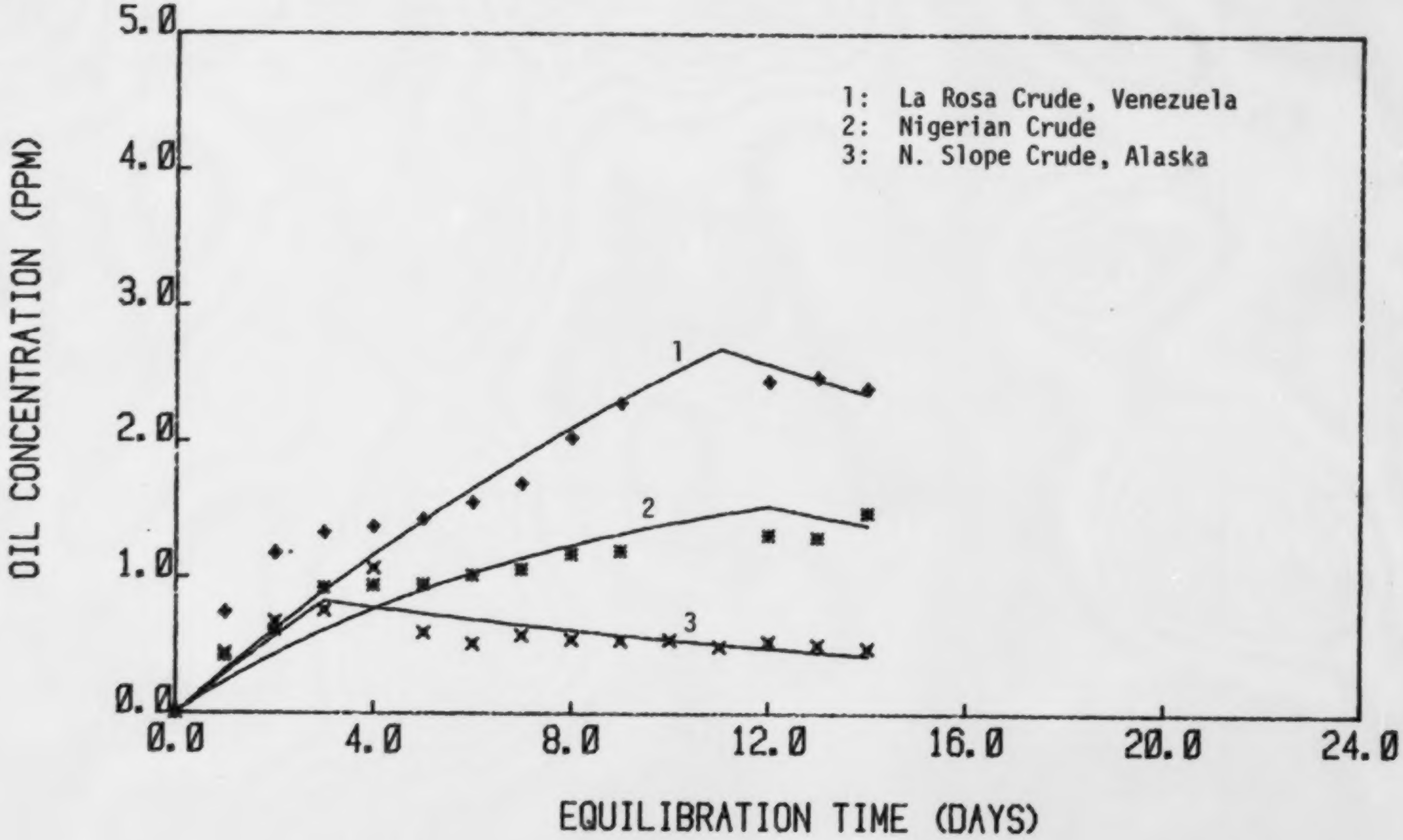

Figure 19. Comparison of Profiles of Dissolution Model and Experimental Data for Nigerian, Alaskan and La Rosa Crudes - Salt Water

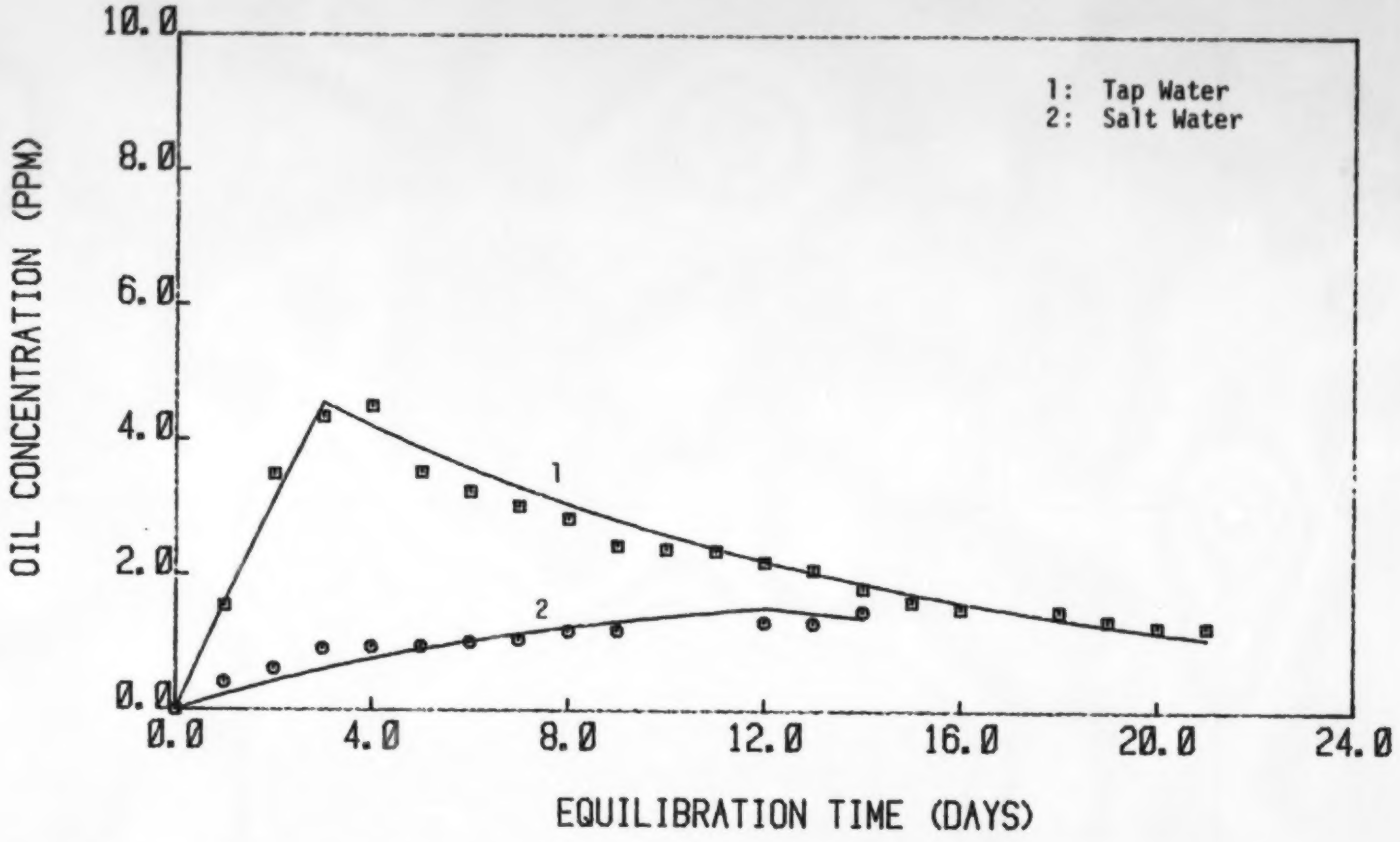

Figure 20. Comparison of Profiles of Dissolution Model and Experimental Data for Nigerian Crude

The rate of dissolution in water of some crude oils and petroleum-based products has been investigated in open static tests. The tests correspond to an unlikely worse case of an oil spill, such that the oil completely covers the water surface. The experimental data suggests that the dissolution process can be divided into two phases. Initially, soluble and volatile organics diffuse into the underlying water; later, some volatile materials evaporate from solution. Thus, the dissolution process is influenced by evaporation in the final stages of equilibration. The amounts of these hydrocarbon species vary according to the composition of the oil, hence, variations exist in maximum solubilities, times to attainment, and dissolution rates. A segmented dissolution model has been applied successfully to correlate the experimental data of the oils. Although the goodness-of-fit of the dissolution model to the experimental data varies, a model based on the two processes has been shown to be capable of reasonable predictions of the solubilities of different oils, as a function of time, in water below a surface slick.

In general, the results of solubility measurements indicate that these oils exhibit low solubilities in water. The processed oils, #2 and #6 fuels, are less soluble than the crude oils. The solubility behavior of oils depends on their chemical composition. For fuel oils, the extent of refinery processing and additives are important factors affecting solubility. The data show that maximum concentrations were not achieved by all the oils after equivalent periods of contact. In spite of variations in maximum solubility levels and times to attainment, the experimental data show similar trends.

The results of the dissolution studies give probable oil concentration levels in the water immediately under a surface slick, when these oils are spilled on water. Oil concentrations are low and may not be hazardous to marine organisms when exposure is limited. Concentration levels may be dangerous when oils attain maximum solubilities in water. A class of marine organisms which has adapted to the sea surface environment is neuston. The solubility limits established for these oils are important to bioassay studies of the toxicity of oils to neuston. Oil concentrations will be lower in sea water. Also, water movements at sea will continuously decrease oil concentration by dilution. In contrast, the dissolved organic matter in the surface microlayers of the sea will increase oil concentration by solubilization.

SPREADING

The rates of spreading of 12 oils were investigated. The experimental runs consisted of spilling specific volumes of oil onto calm tap water. Four different volumes of each oil were spilled at different flow rates. The effects on spreading of several parameters, such as the volume of oil spilled, duration of spill and physical properties of the oils, i.e. viscosity, density, surface tension and interfacial tension between oil and water, were investigated. These parameters are important in determining the increase with time of the area of an oil slick spreading on calm water. Water temperature is a factor in the rates of spreading of oils but it was not investigated in this study because the effect of temperature should be determined by its influence on the properties of the oil and water phases. The effect of temperature will be proportional to changes in the values of the physical properties of the two phases. The data generated in each experimental run include areal extents of the oil as a function of the time of spreading. Photographic techniques were used and the areas covered by the oils were measured from photographic images.

All the oils did not spread uniformly and several slicks developed regions with varying thicknesses of oil. In some cases, subjective judgment was used to determine the areal extent of a slick if its profile was not properly defined in the photographic prints. Spreading patterns vary for different oils and there is no preference for elliptic or circular geometries. The initial configurations of a slick during the initiation of spreading and the final profile at the end of an experiment are influenced by the rate of oil discharge, the duration of the spill, thermal convection currents in the water column, properties of the oil and spreading forces. The configurations and areas of slicks may vary even when the slicks are formed by the same oil and under the same conditions.

Spreading equations were derived to correlate experimental data. The development of these equations parallels Fay's work and yields four spreading equations: surface-tension/viscous (STV), surface-tension/inertia (STI), gravity/viscous (GV), and gravity/inertia (GI). Each spreading equation defines a spreading regime in which only two opposing forces dominate the spreading behavior of a slick. The equation for each regime is then derived by equating two forces, one of which accelerates spreading and the other retarding spreading. The dependent variable in each equation is the area covered by the spreading slick and the independent variables include the properties of the oil and water phases. This information is usually available at sites of spills or can be determined experimentally. Each equation contains an empirical constant.

Experimental data from spreading studies are presented in Appendix D. The spreading equations were fitted to experimental data to estimate the values of the empirical coefficients. The final values of the coefficients and the regression statistics are summarized in Tables 10 to 21. The correlation coefficients indicate the models are capable of fitting experimental data with varying accuracies. In general, the order of the goodness-of-fit of the spreading equations from the best to the worst is

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GV > STV > GI > STI. As expected the fit with the surface-tension/inertia model was the worst; this model predicts that the area of spreading is independent of the volume of oil spilled. Thus, this equation is not acceptable as a model for predicting variation of the area covered by an oil slick with time.

TABLE 10

Summary of Coefficients of Spreading Equations for Arzew Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	15.695	0.966
	50	12.356	0.9745
	75	11.400	0.9769
	100	10.289	0.9580
2. Surface-Tension/Inertia			
	25	0.0392	0.5550
	50	0.0466	0.5776
	75	0.0549	0.6040
	100	0.0603	0.579
3. Gravity/Viscous			
	25	25.922	0.9895
	50	18.274	0.9937
	75	15.908	0.9935
	100	13.800	0.9720
4. Gravity/Inertia			
	25	3.208	0.8514
	50	2.541	0.8695
	75	2.342	0.8804
	100	2.133	0.8585

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TABLE 11

Summary of Coefficients of Spreading Equations for Brass River Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous	25	7.869	0.9757
	50	4.462	0.9636
	75	4.533	0.9479
	100	3.747	0.9860
2. Surface-Tension/Inertia	25	0.0183	0.7792
	50	0.0132	0.5845
	75	0.0169	0.6096
	100	0.0189	0.7843
3. Gravity-Viscous	25	13.559	0.9528
	50	7.136	0.9847
	75	6.901	0.9656
	100	5.289	0.9739
4. Gravity/Inertia	25	1.705	0.9718
	50	0.905	0.8589
	75	0.909	0.8547
	100	0.799	0.9716

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TABLE 12

Summary of Coefficients of Spreading Equations for Alaskan Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	59.989	0.9953
	50	49.778	0.9785
	75	28.064	0.9921
	100	28.304	0.9847
2. Surface-Tension/Inertia			
	25	0.0772	0.6791
	50	0.0908	0.6563
	75	0.0664	0.6582
	100	0.0775	0.6426
3. Gravity/Viscous			
	25	68.238	0.9986
	50	52.281	0.9901
	75	27.060	0.9987
	100	26.332	0.9955
4. Gravity/Inertia			
	25	5.175	0.9278
	50	4.154	0.8961
	75	2.402	0.9176
	100	2.396	0.9024

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TABLE 13

Summary of Coefficients of Spreading Equations for Iranian Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	34.650	0.9853
	50	24.920	0.7905
	75	20.314	0.9676
	100	18.990	0.9621
2. Surface-Tension/Inertia			
	25	0.0573	0.6355
	50	0.0594	0.5918
	75	0.0609	0.5906
	100	0.0670	0.5871
3. Gravity/Viscous			
	25	47.472	0.9966
	50	30.818	0.9898
	75	23.619	0.9873
	100	21.139	0.9817
4. Gravity/Inertia			
	25	4.399	0.9003
	50	3.126	0.8684
	75	2.544	0.8648
	100	2.373	0.8584

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TABLE 14

Summary of Coefficients of Spreading Equations for Sahara Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	41.544	0.9665
	50	28.351	0.9415
	75	17.955	0.9739
	100	20.108	0.9044
2. Surface-Tension/Inertia			
	25	0.0616	0.5564
	50	0.0618	0.5437
	75	0.0511	0.5973
	100	0.0642	0.5526
3. Gravity/Viscous			
	25	67.098	0.9905
	50	41.554	0.9666
	75	24.490	0.9916
	100	26.951	0.9226
4. Gravity/Inertia			
	25	6.555	0.8525
	50	4.415	0.8242
	75	2.845	0.8746
	100	3.056	0.7904

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TABLE 15

Summary of Coefficients of Spreading Equations for Nigerian Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	10.300	0.9674
	50	8.342	0.9920
	75	6.459	0.9974
	100	7.486	0.9849
2. Surface-Tension/Inertia			
	25	0.0182	0.8198
	50	0.0193	0.6820
	75	0.0198	0.7542
	100	0.0280	0.9005
3. Gravity/Viscous			
	25	15.232	0.9324
	50	11.492	0.9987
	75	8.287	0.9907
	100	9.429	0.9727
4. Gravity/Inertia			
	25	1.584	0.9868
	50	1.207	0.9242
	75	0.954	0.9649
	100	1.094	0.9944

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TABLE 16

Summary of Coefficients of Spreading Equations for #2 Fuel Oil

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	39.609	0.9873
	50	18.708	0.9755
	75	15.165	0.9899
	100	15.308	0.9770
2. Surface-Tension/Inertia			
	25	0.0905	0.6357
	50	0.0614	0.6014
	75	0.0656	0.7133
	100	0.0763	0.6801
3. Gravity/Viscous			
	25	60.742	0.9940
	50	26.121	0.9931
	75	20.133	0.9954
	100	19.518	0.9856
4. Gravity/Inertia			
	25	7.008	0.9082
	50	3.247	0.8778
	75	2.631	0.9260
	100	2.628	0.9002

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TABLE 17

Summary of Coefficients of Spreading Equations for #6 Fuel Oil

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	5.552	0.9846
	50	6.440	0.9425
	75	5.219	0.8590
	100	6.329	0.9448
2. Surface-Tension/Inertia			
	25	0.0021	0.7443
	50	0.0041	0.9012
	75	0.0045	0.9658
	100	0.0059	0.8994
3. Gravity/Viscous			
	25	4.709	0.9680
	50	4.809	0.8960
	75	3.607	0.7998
	100	4.288	0.9090
4. Gravity/Inertia			
	25	0.182	0.9598
	50	0.220	0.9977
	75	0.182	0.9595
	100	0.213	0.9867

TABLE 18

Summary of Coefficients of Spreading Equations for 8% Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	30.991	0.9141
	50	27.293	0.9917
	75	25.342	0.9987
	100	25.264	0.9907
2. Surface-Tension/Inertia			
	25	0.0488	0.9111
	50	0.0567	0.8410
	75	0.0644	0.7748
	100	0.0730	0.7715
3. Gravity/Viscous			
	25	39.925	0.8634
	50	32.973	0.9780
	75	28.636	0.9918
	100	27.895	0.9905
4. Gravity/Inertia			
	25	3.657	0.9878
	50	3.024	0.9887
	75	2.791	0.9700
	100	2.700	0.9433

TABLE 19

Summary of Coefficients of Spreading Equations for Lagunillas Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	21.614	0.8623
	50	13.338	0.8745
	75	35.032	0.9761
	100	35.032	0.9761
2. Surface-Tension/Inertia			
	25	0.0112	0.9555
	50	0.0102	0.9549
	75	0.0351	0.8423
	100	0.0351	0.8423
3. Gravity/Viscous			
	25	19.840	0.7976
	50	11.085	0.8149
	75	26.719	0.9470
	100	26.719	0.9470
4. Gravity/Inertia			
	25	0.953	0.9696
	50	0.587	0.9756
	75	1.462	0.9949
	100	1.462	0.9949

TABLE 20

Summary of Coefficients of Spreading Equations for La Rosa Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous			
	25	61.194	0.9835
	50	56.427	0.9754
	75	57.586	0.9839
	100	53.202	0.9465
2. Surface-Tension/Inertia			
	25	0.0798	0.7458
	50	0.1001	0.6488
	75	0.1327	0.6840
	100	0.1378	0.6597
3. Gravity/Viscous			
	25	60.062	0.9662
	50	51.190	0.9864
	75	48.649	0.9884
	100	44.097	0.9540
4. Gravity/Inertia			
	25	4.261	0.9636
	50	3.739	0.8920
	75	3.869	0.9163
	100	3.442	0.8620

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TABLE 21

Summary of Coefficients of Spreading Equations for Suniland Crude

Equation	Vol.	K	R^2
1. Surface-Tension/Viscous	25	52.768	0.9516
	50	30.937	0.9958
	75	27.396	0.9818
	100	24.414	0.9852
2. Surface-Tension/Inertia	25	0.0701	0.5720
	50	0.0673	0.7414
	75	0.0717	0.6645
	100	0.0751	0.6569
3. Gravity/Viscous	25	73.803	0.9726
	50	38.545	0.9918
	75	32.233	0.9896
	100	27.386	0.9999
4. Gravity/Inertia	25	6.179	0.8437
	50	3.742	0.9527
	75	3.254	0.9060
	100	2.908	0.9083

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The values of the coefficients differ for each oil and spreading regime. Within each spreading regime slight to large differences can be seen in the values of the coefficients for the four oil volumes spilled. These differences are caused by experimental error due to variations in thermal convection currents in the water and, perhaps, air motions which are unavoidable even in the laboratory environment. It is probable that for each spreading regime, the mean of the four coefficients is a more accurate value for the empirical constant.

The experimental data and predictions by the four spreading equations are given in Figures 21 to 32 for #2 fuel oil, Nigerian and Alaskan crudes. The data and model profiles show that oil slicks spread faster initially and spread more slowly as the slicks age.

The effects of oil properties, i.e. density, viscosity, surface tension and interfacial tension between oil and water can be judged from the spreading equations. Increases in density and viscosity have negative effects on the spreading behavior of oils. The net effect of surface tension varies according to whether it is positive (accelerates spreading) or negative (retards spreading). Data for #6 fuel oil and Lagunillas crude show that viscous oils spread more slowly than less viscous oils. As the ratio of the density of oil-to-water decreases, spreading rate increases. Since spreading of oils on water persists longer than the duration of the spill, the initial effect of the rate of oil discharge is cancelled by the total volume of the oil spilled. Therefore, the rate of discharge of oil is important in the early stages of a spill and in situations where the oil is discharged continuously, e.g., oil seeps.

The mathematical models used here are valid only for spreading on calm seas. The results of the experiments have shown that, even for this simple situation,oils behave differently. Information on the behavior of a greater variety of oil types is needed. In the open sea, gross oil transport commences almost immediately after oil is spilled. The transport processes due to turbulence created by wind, current, wave and tidal forces will be superimposed on natural spreading. The rates of these processes are at present difficult to quantify, however, these modes of transport are of importance in evaluating the potential damage to marine ecosystems by oil slicks.

CHEMICAL DISPERSION

When oil slicks are agitated by turbulent forces at sea, they break up into small droplets that disperse into the water. The formation and dispersal of oil droplets can be aided by application of chemical dispersants to the slick. Thus, information on the mechanisms leading to dispersion of droplets is

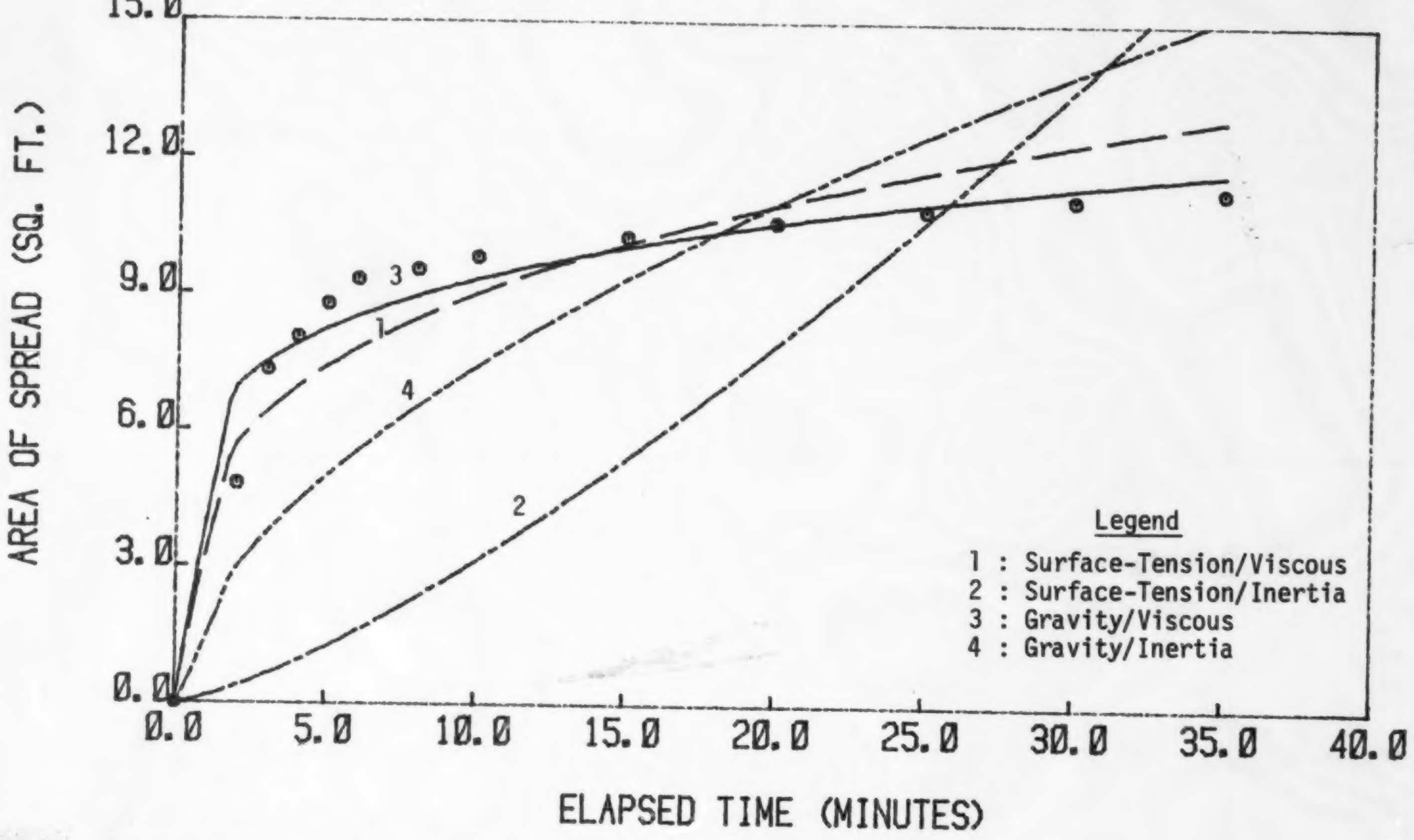

Figure 21. Comparisons of Experimental Data and Spreading Equations for #2 Fuel Oil (25 mls)

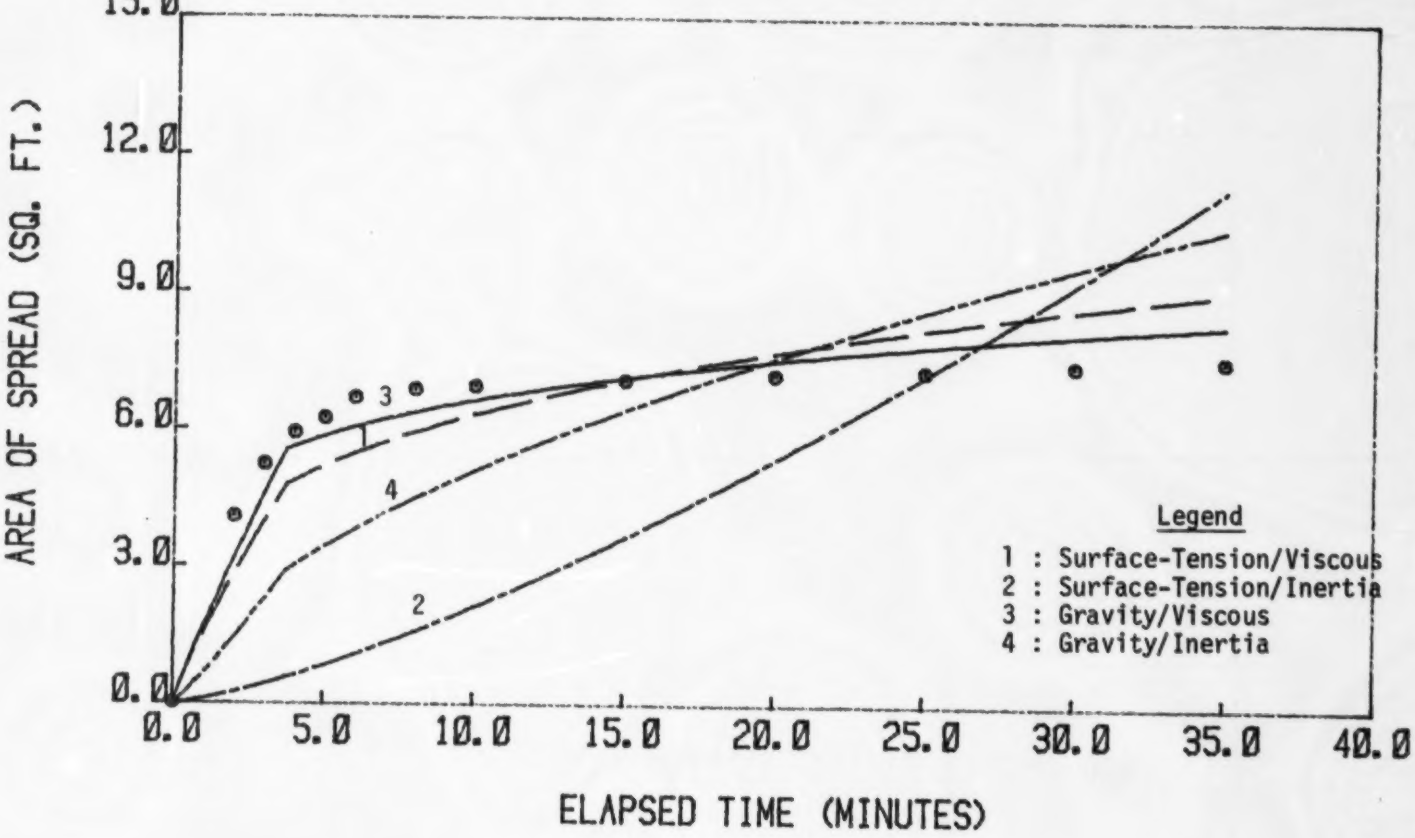

Figure 22. Comparisons of Experimental Data and Spreading Equations for #2 Fuel Oil (50 mls)

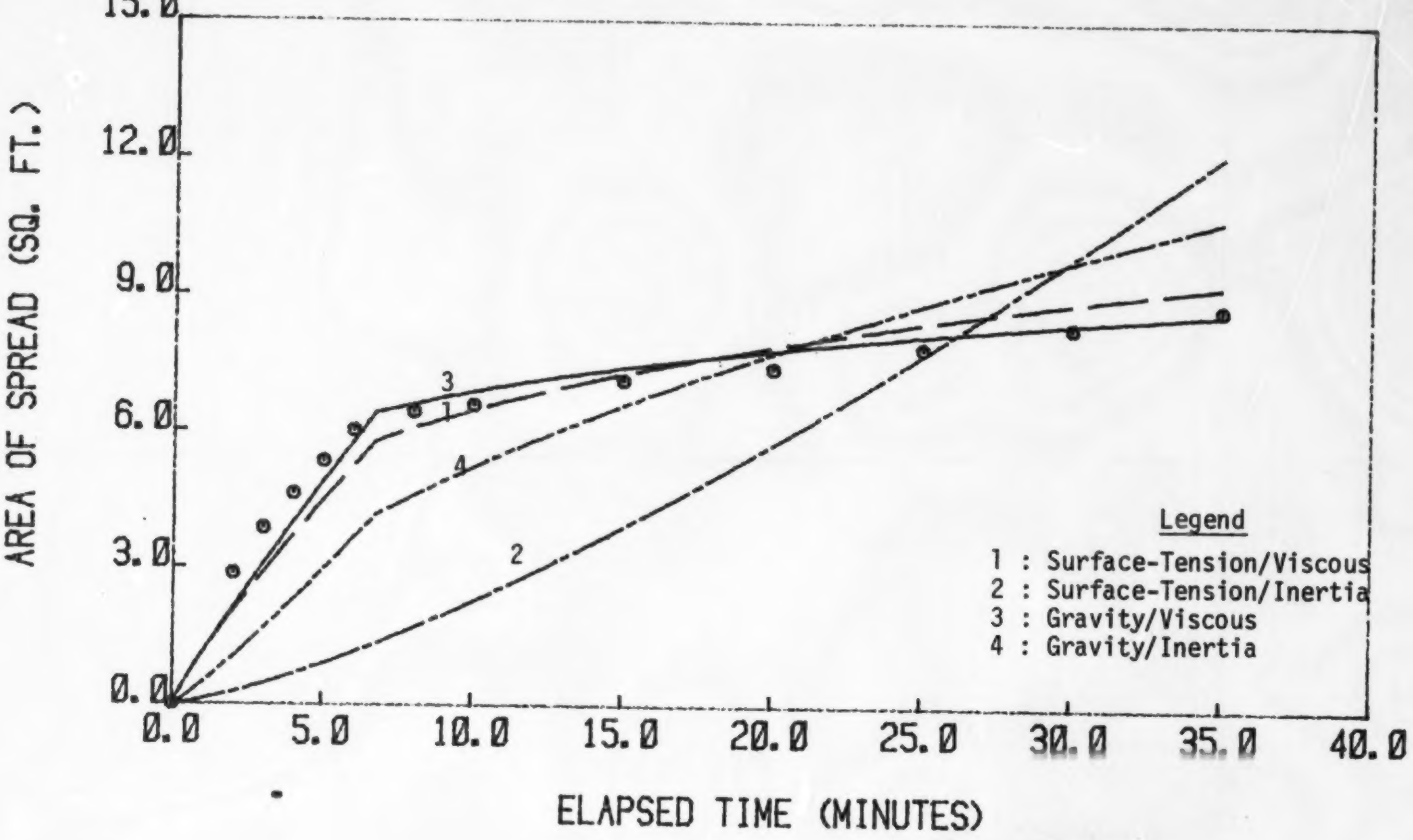

Figure 23. Comparisons of Experimental Data and Spreading Equations for #2 Fuel Oil (75 mls)

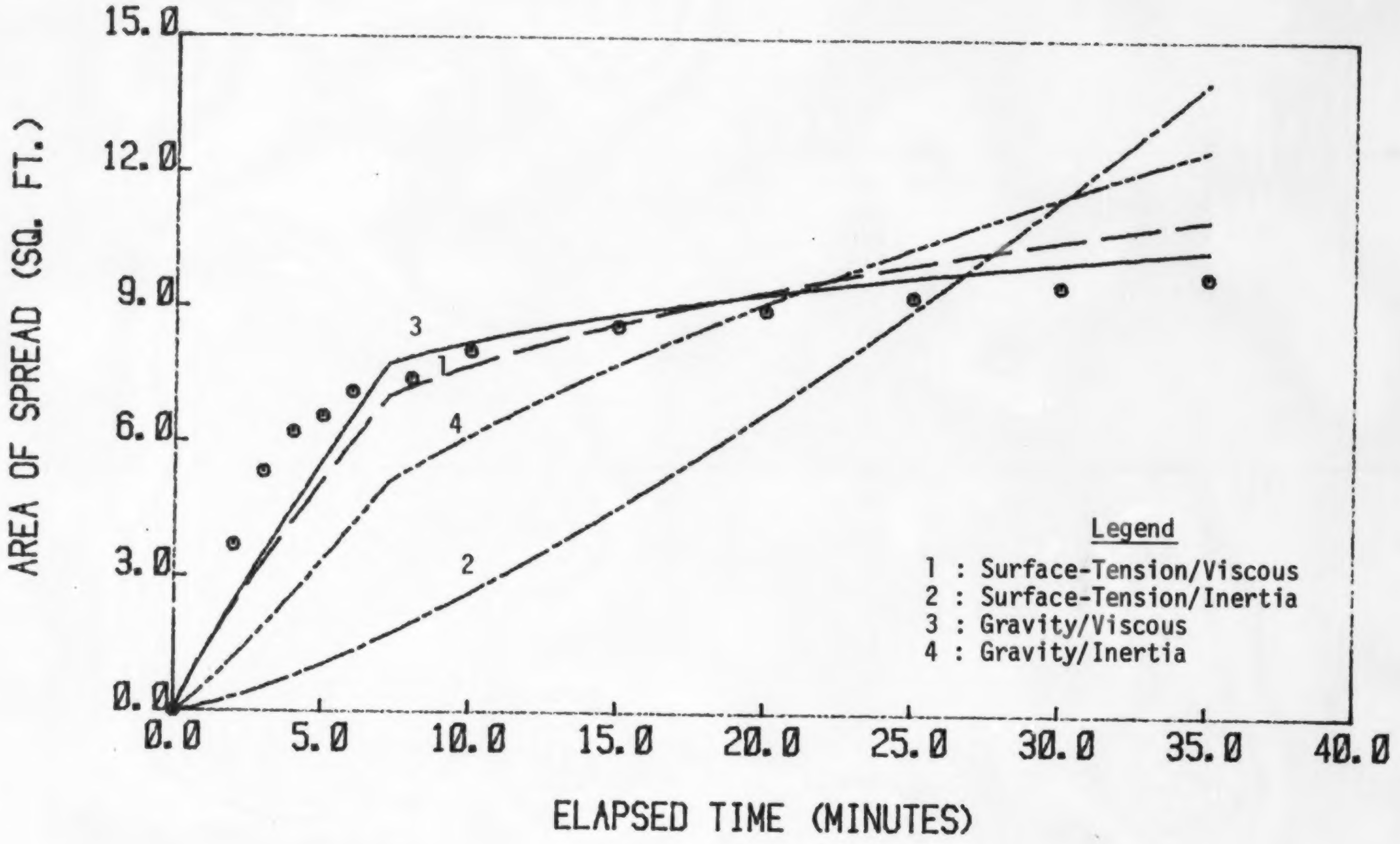

Figure 24. Comparisons of Experimental Data and Spreading Equations for #2 Fuel Oil (100 mls)

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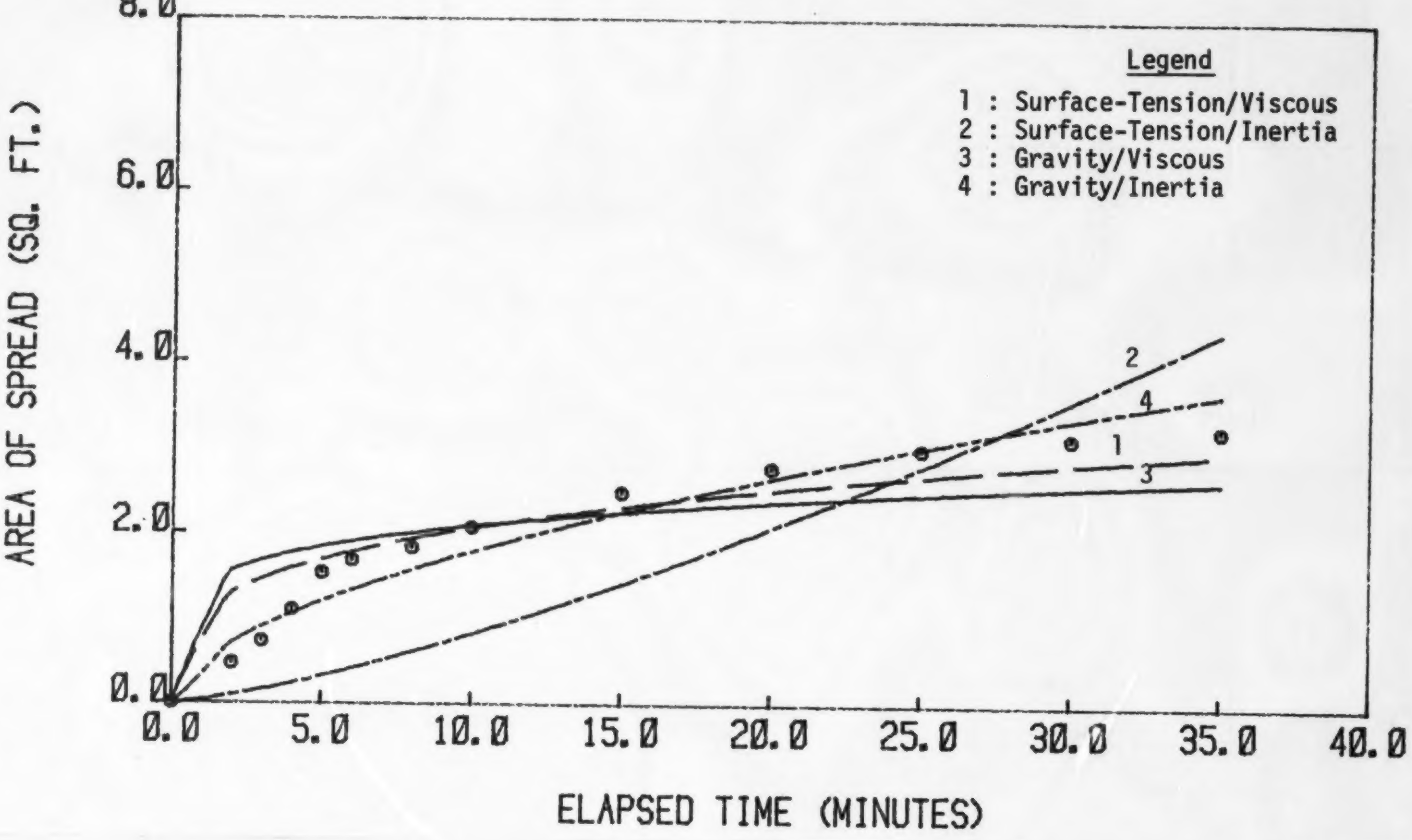

Figure 25. Comparisons of Experimental Data and Spreading Equations for Nigerian Crude (25 mls)

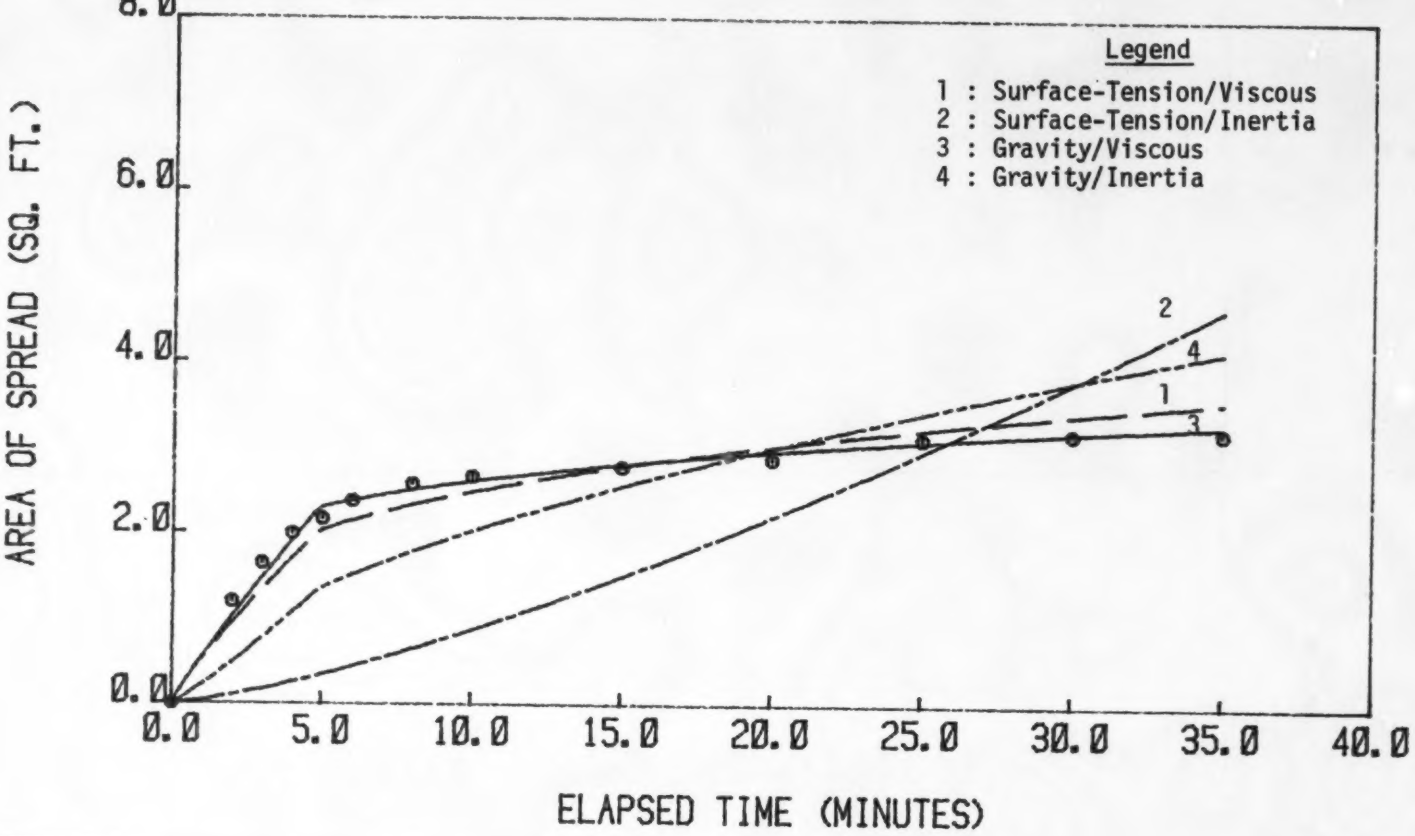

Figure 26. Comparisons of Experimental Data and Spreading Equations for Nigerian Crude (50 mls)

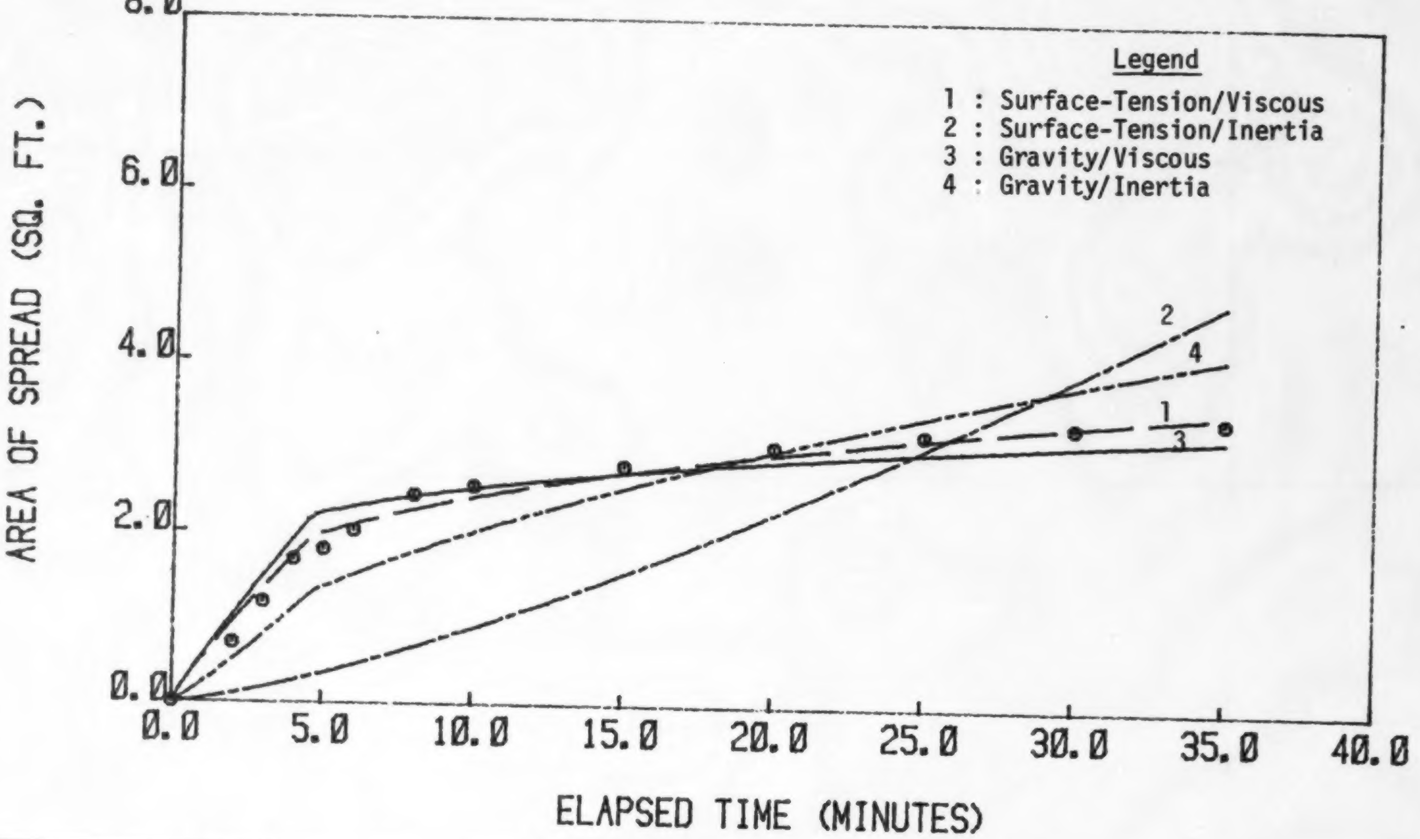

Figure 27. Comparisons of Experimental Data and Spreading Equations for Nigerian Crude (75 mls)

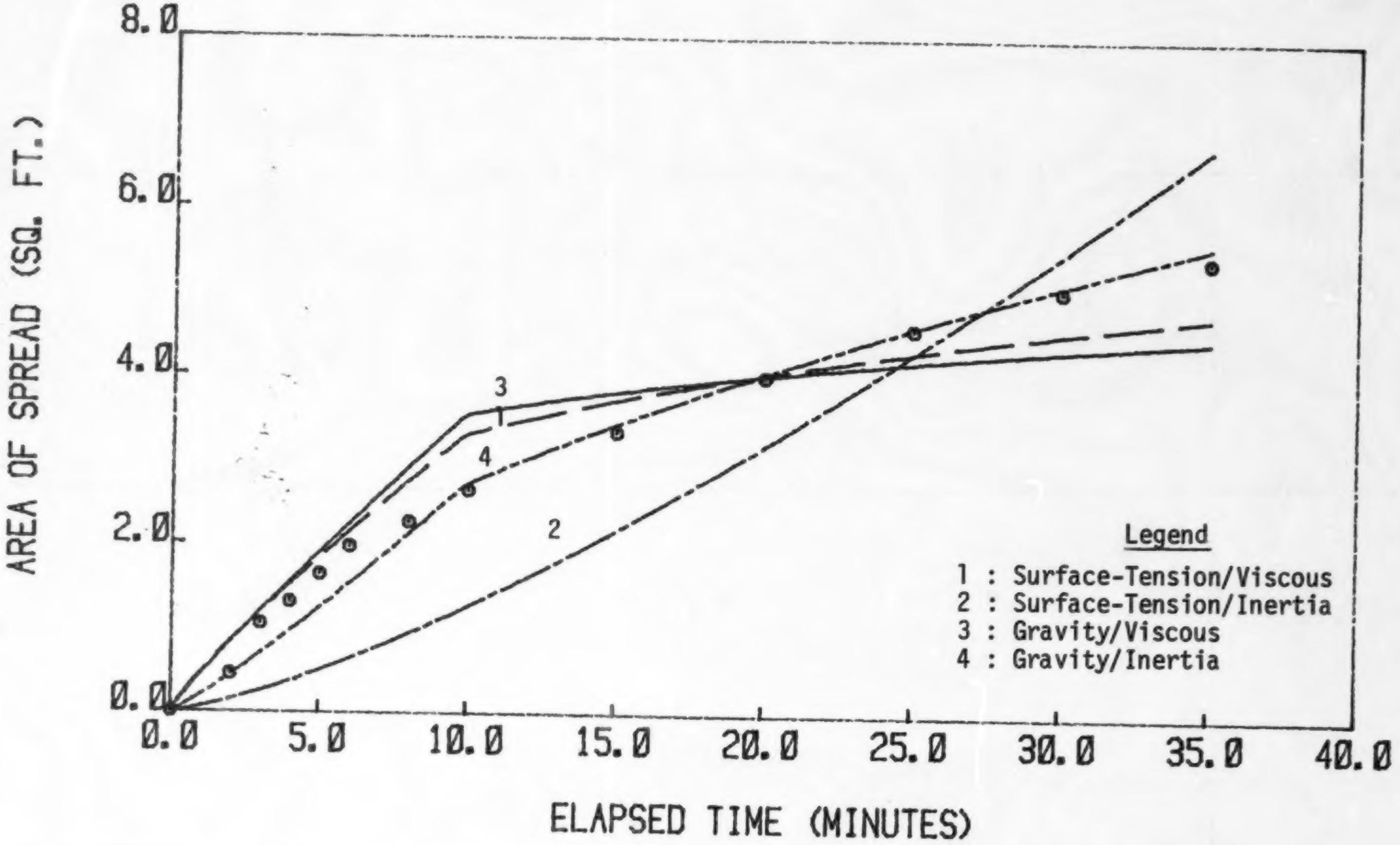

Figure 28. Comparisons of Experimental Data and Spreading Equations for Nigerian Crude (100 mls)

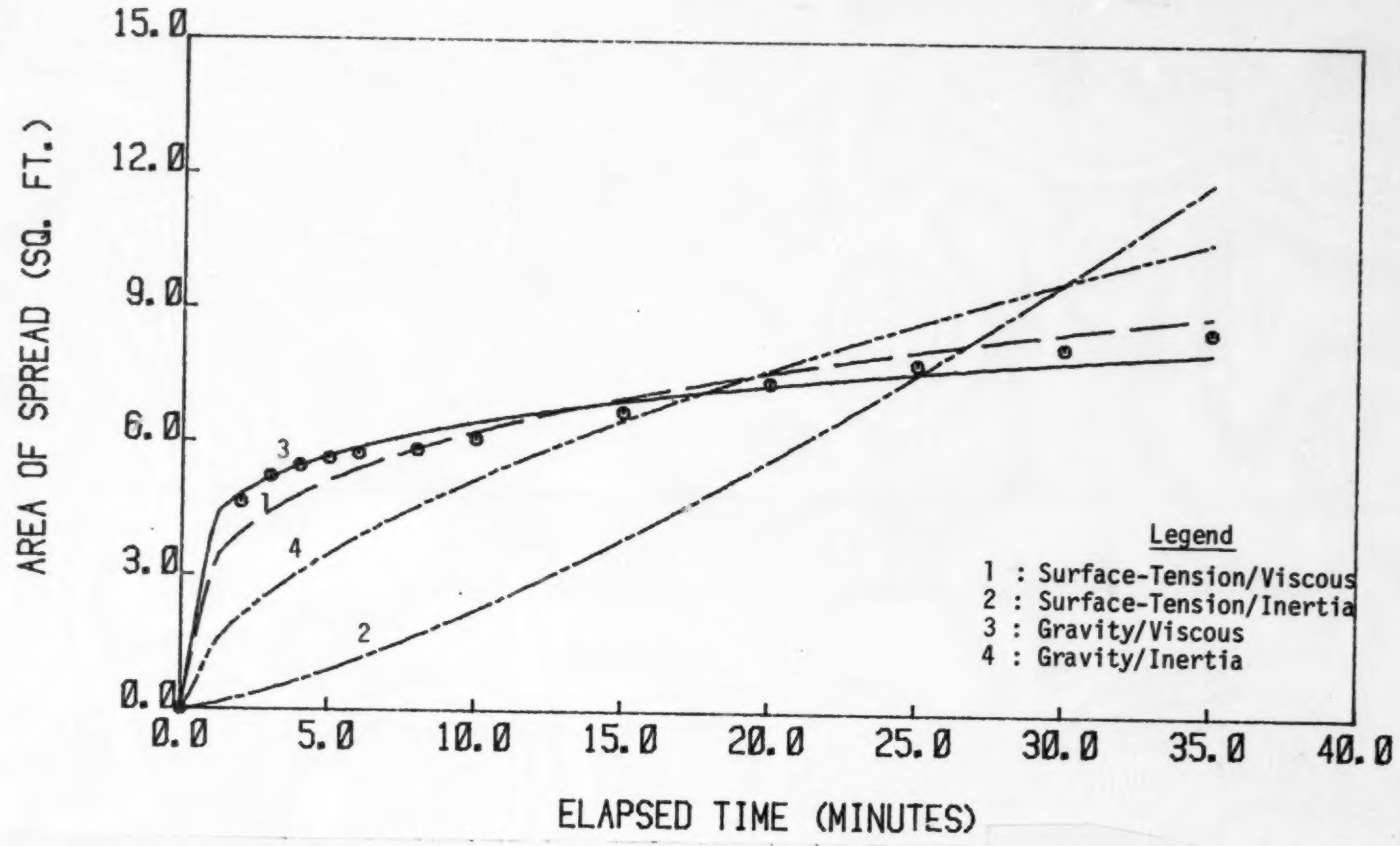

Figure 29. Comparisons of Experimental Data and Spreading Equations for Alaskan Crude (25 mls)

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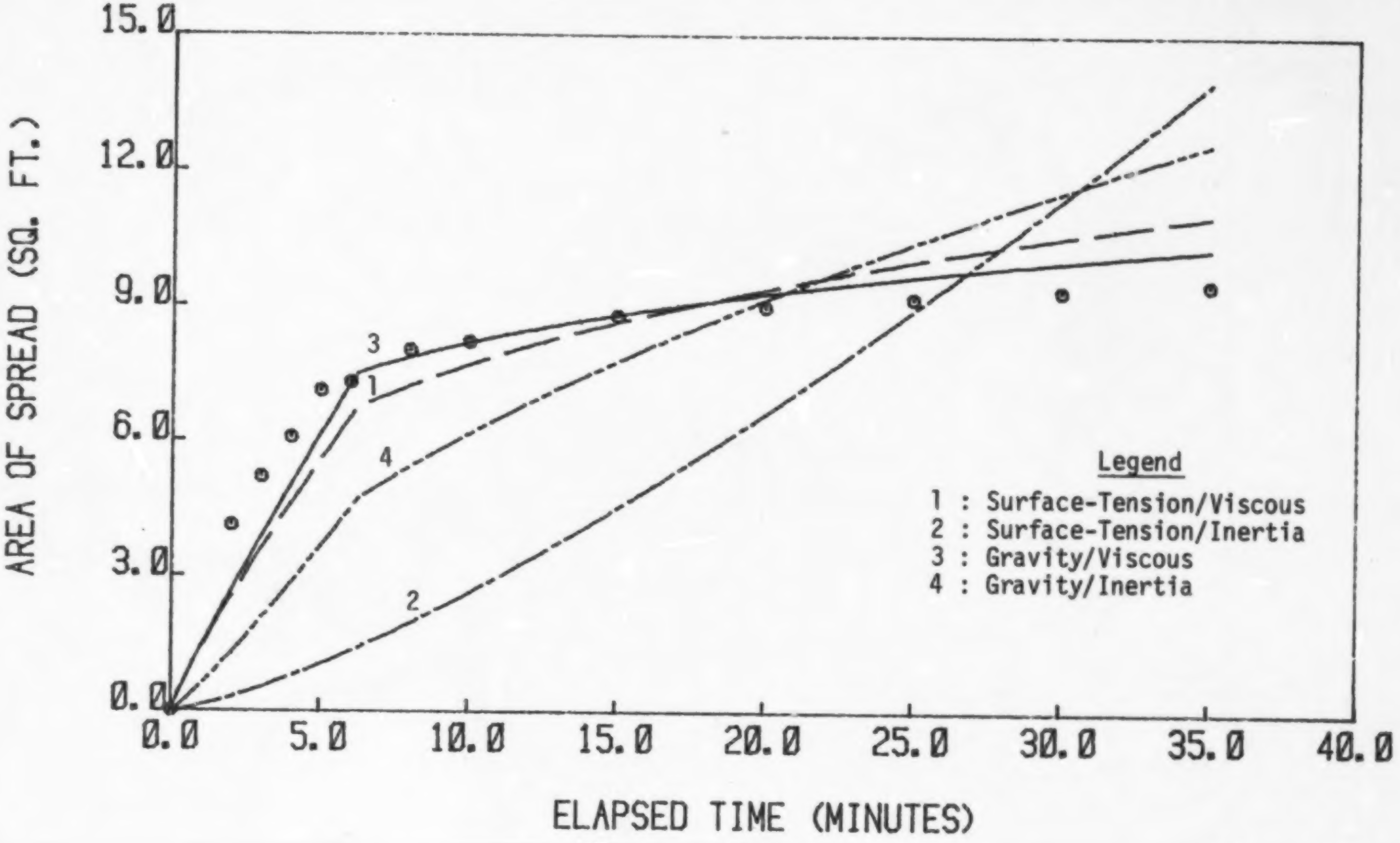

Figure 30. Comparisons of Experimental Data and Spreading Equations for Alaskan Crude (50 mls)

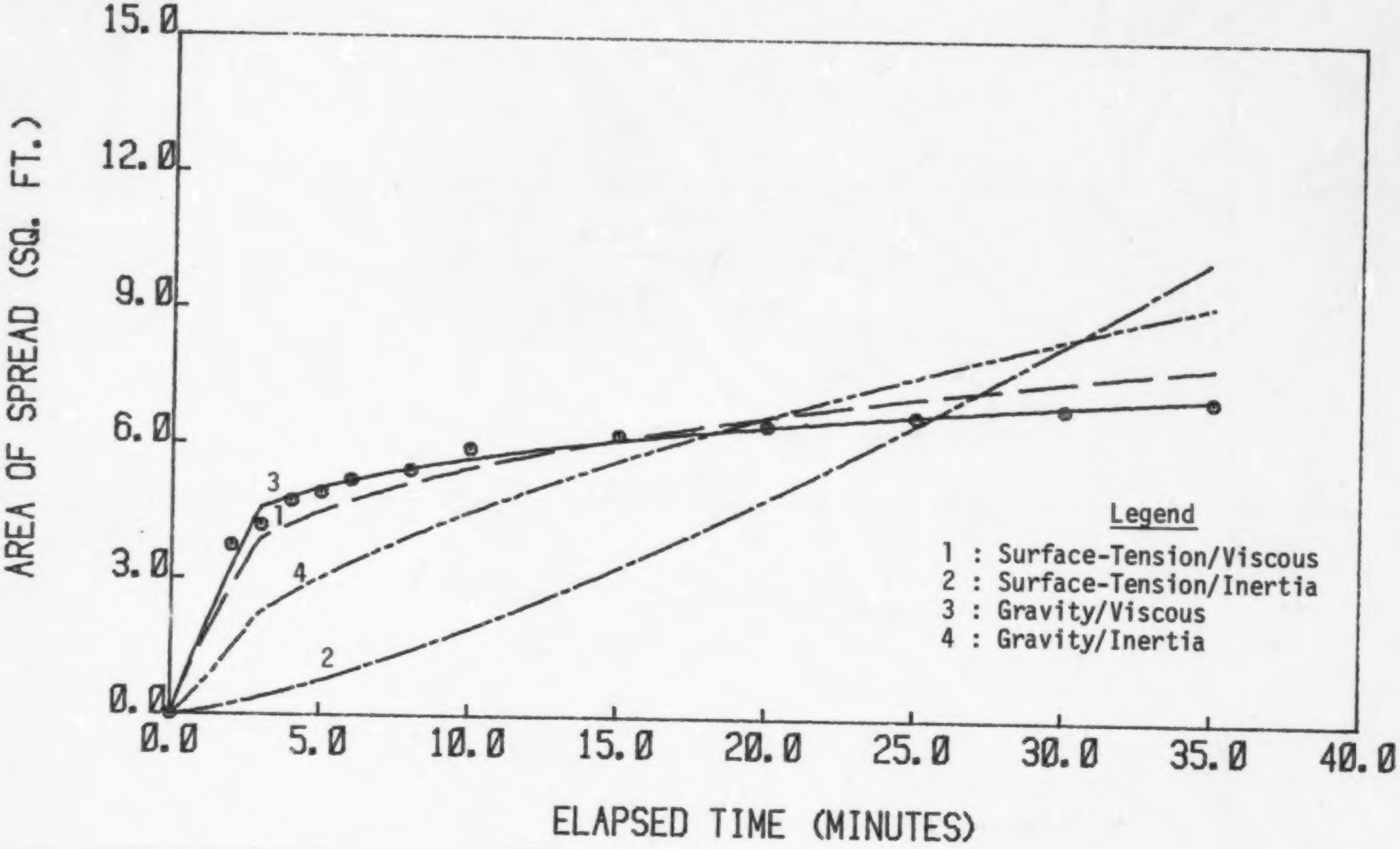

Figure 31. Comparisons of Experimental Data and Spreading Equations for Alaskan Crude (75 mls)

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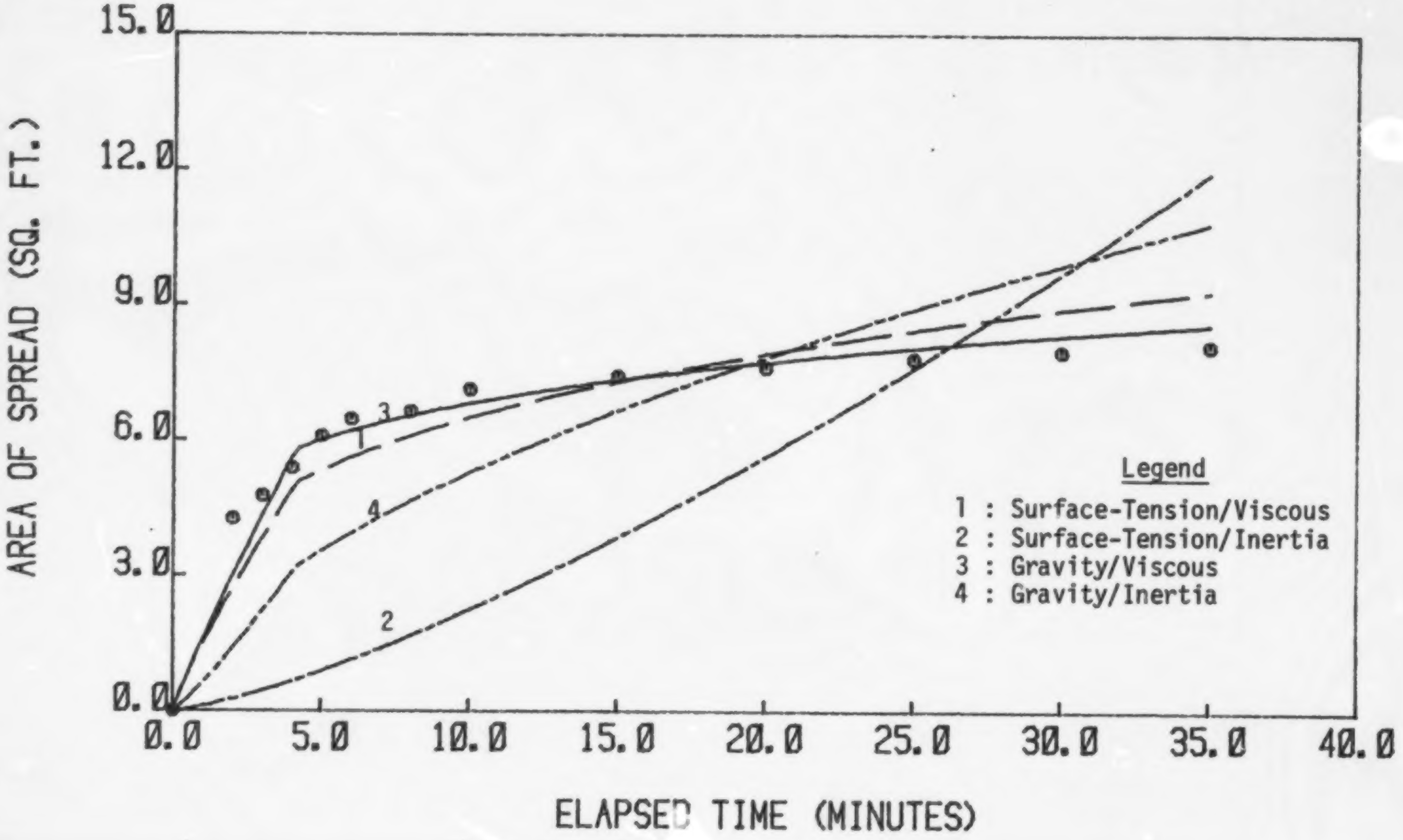

Figure 32. Comparisons of Experimental Data and Spreading Equations for Alaskan Crude (100 mls)

essential to planning appropriate clean-up operations, using commercially available dispersants.

This study has identified the principal and secondary mass transfer processes that are important in chemical dispersion. A theoretical formulation has been proposed to explain these mechanisms of chemical dispersion. This theory is based on detergency and catalysis concepts. Mathematical models were derived to quantify the principal mechanisms according to the steps that are rate limiting. The models must be judged on their merits as they were not verified by experimental data, due to lack of accurate input data. Because of the variety of commercially available dispersants, knowledge of the mechanisms of chemical dispersion is essential to establishing a rationale for dispersant selection. This work has identified these mechanisms.

As this study progressed, the limitations of modeling became apparent. For example, the chemical structure and the degree of association or micellization of surface-active compounds in commercial dispersant preparations must be known. This information is proprietary. The properties of the surfactants are useful for determining the rate controlling steps. This study underscores the importance of basic data utilizing known surface active compounds in free form and mixtures of surfactants. The results of the experimental data from dispersion tests using 5 commercial dispersants and 3 oils are discussed next.

Current practices in chemical dispersion tests report the effectiveness of chemical dispersants in terms of the percent dispersion. The percent dispersion is based on the concentration of oil in solution, following violent agitation of an oil/water/dispersant system, as a fraction of the concentration of oil that would result if all the oil were dispersed in the water. This practice is not followed here because it has little merit and it does not reflect accurately the efficiency of dispersants. A brief explanation follows.

Usually, dispersants are formulated in hydrocarbon or aqueous solvents. Hydrocarbon-base dispersants have some advantages over aqueous-base dispersants. For instance, hydrocarbon solvents are easily miscible with oil slicks. This may lead to faster dispersion of oil slicks.

Furthermore, the sources of hydrocarbon in an oil/water/dispersant system are the slick material and the dispersant. Thus, a hydrocarbon-base dispersant will contribute a larger amount of hydrocarbon to the system than an aqueous-base dispersant containing the same surface-active compounds. Since commercial dispersants contain a variety of surface-active compounds and additives with hydrocarbon molecules, the fraction of hydrocarbons in different dispersants will vary with the structure of the surface-active compounds (the hydrophobic group), and the concentration of surfactant, hydrocarbon solvent and additives.

A water sample from a dispersion test will contain some hydrocarbon from all the sources. Analytical techniques do not discriminate between the hydrocarbon fractions contributed by the hydrocarbon solvent, the hydrophobic group of the dispersant, and the oil slick. Surely, a hydrocarbon-base dispersant will show higher oil levels in aqueous solutions even though the efficiency may be identical to the aqueous-base dispersant containing the same surface-active compounds and additives. The effect of the type of solvent on the efficiency of dispersants could be partially resolved through use of calibration curves based on oil and dispersant mixtures.

Even when the structure of the surfactant and its concentration in the dispersant solution are known, it is not easy to determine the fraction of oil introduced into solution by treating the surface slick. The possible sinks for surfactants in the system are a) the bulk oil phase and dispersant solution, b) adsorption at the oil/water interface, as free or mixed micelles, and c) the bulk water phase, as unaggregated molecules or in mixed micelles. It is impossible to determine these concentrations separately. Therefore, development of a meaningful criterion to rank commercial dispersants without information on the composition of the formulations remains a major task.

The trends in experimental data gathered from the dispersion of 3 oils with 5 dispersants under different test conditions will be discussed. Slicks formed by spilling 300 mls of oil were dispersed with dispersants in 1:1, 5:1 and 10:1 oil-to-dispersant ratios. The experimental data have been presented in Appendix E. Figures 33 to 35 are concentration-time profiles for the dispersion of #2 fuel oil with the five products at 1:1, 5:1, and 10:1 oil-to-dispersant ratios, respectively. The maximum oil concentration represents the average oil and dispersant concentration in the bulk fluid immediately after agitation was stopped. An analogy to current practice of using percent efficiency can be made by normalizing the maximum oil concentration by the oil concentration that would result if all the oil was completely dispersed in the volume of the aqueous phase. Therefore, 100% dispersion corresponds to 425 ppm. The profiles show decreases in oil concentration with sampling time for all products. The greatest decrease occurred with product B. Oil concentrations stabilized after about 2 hours. If all the products are assumed to contain equal concentrations of the same solvent, the order of the relative ease of dispersion of #2 fuel oil is given below

O/D Ratio	Dispersion of #2 Fuel Oil
1:1	D > B > A > C > E
5:1	D > A > B > C > E
10:1	D > B = A > C > E

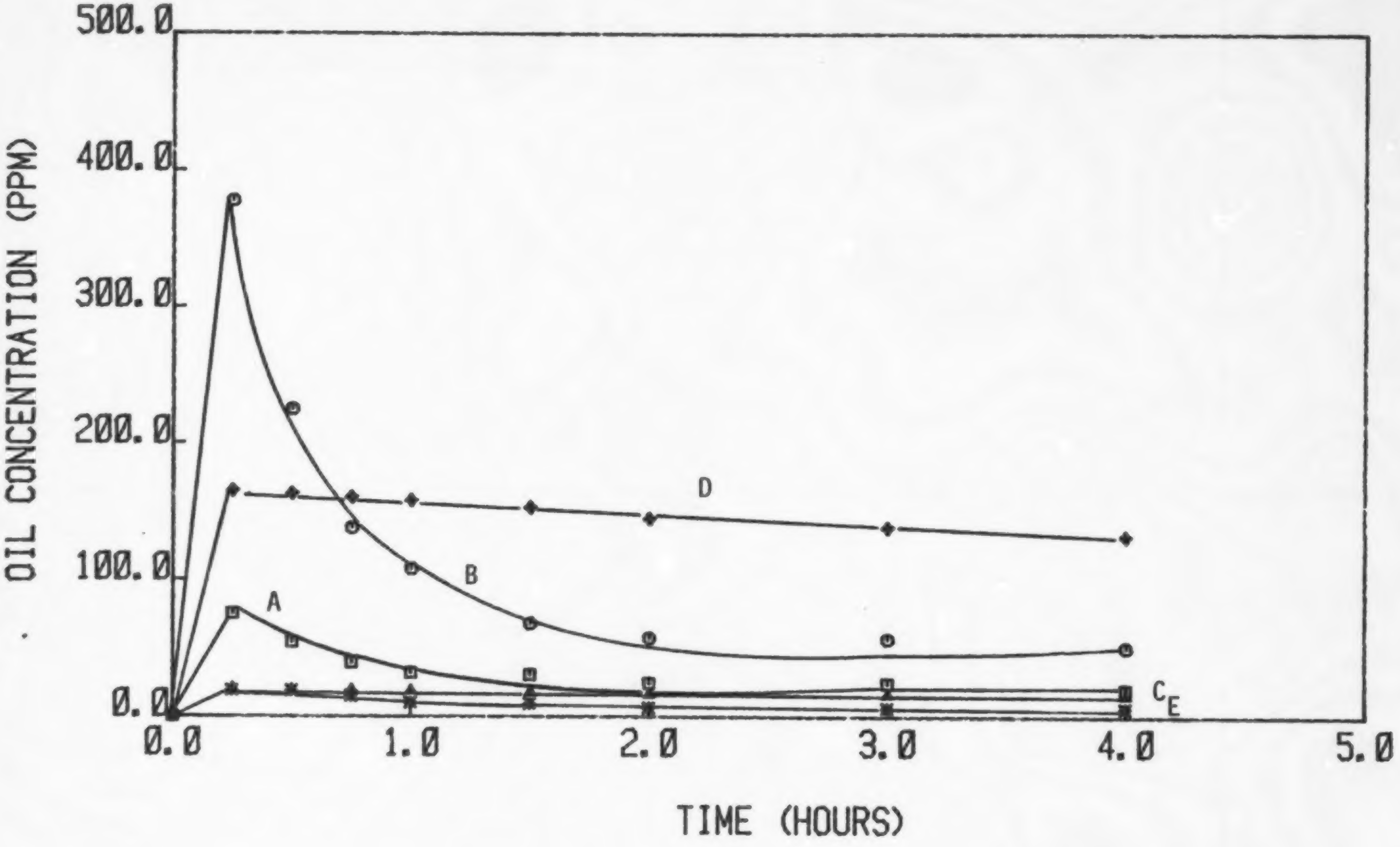

Figure 33. Dispersion of #2 Fuel Oil with Products A, B, C, D and E at 1:1 Oil-to-Dispersant Ratio

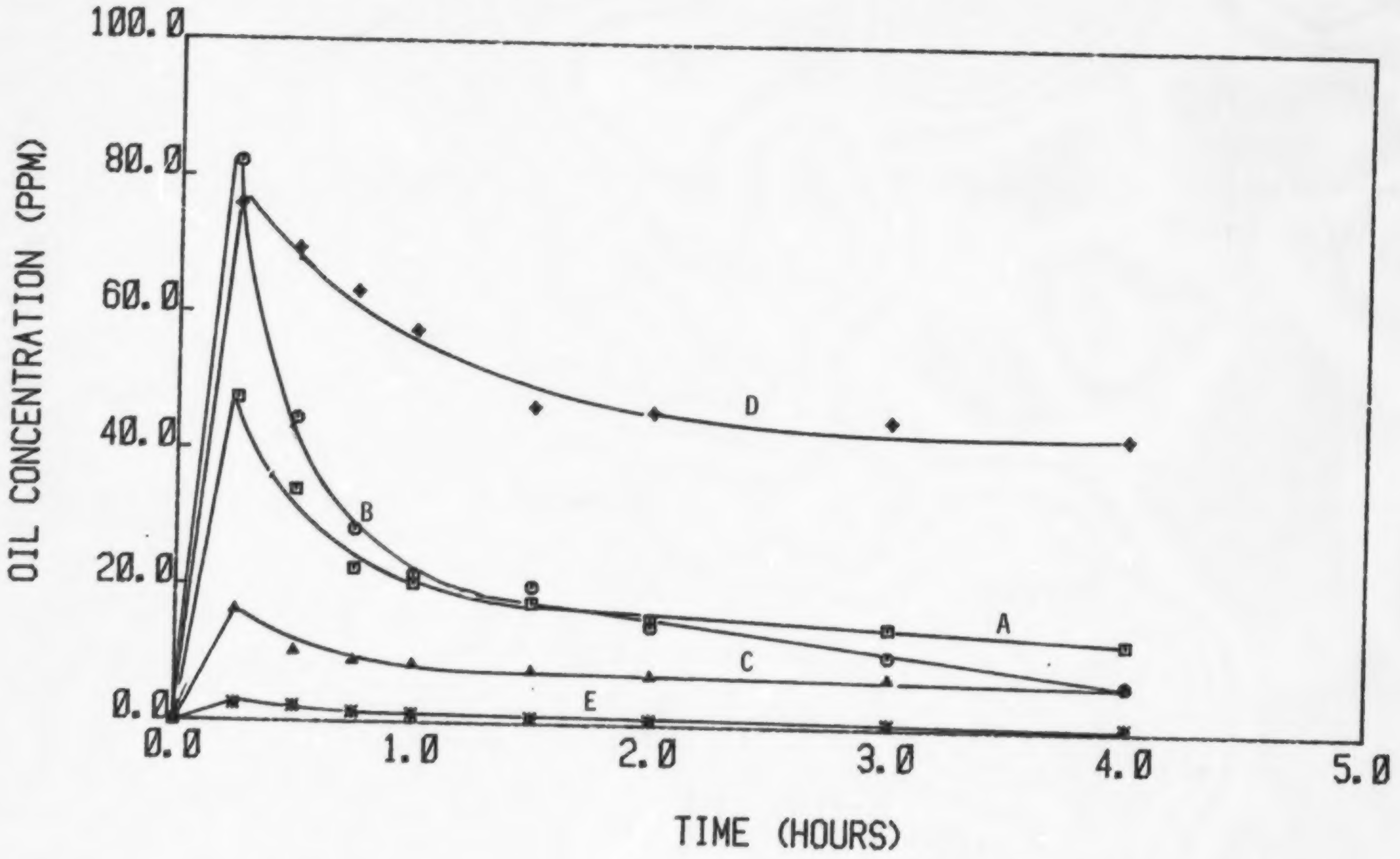

Figure 34. Dispersion of #2 Fuel Oil with Products A, B, C, D, and E at 5:1 Oil-to-Dispersant Ratio

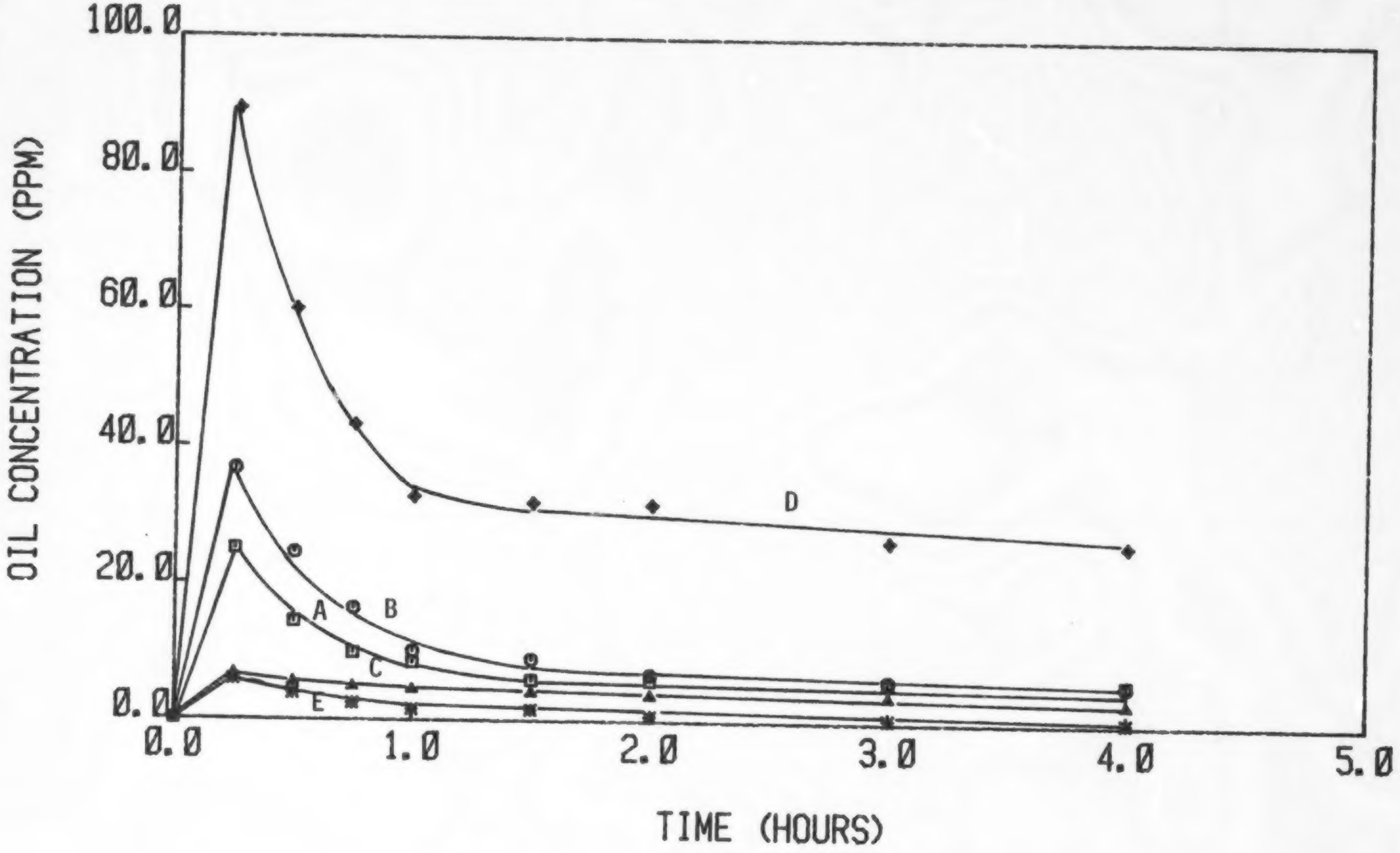

Figure 35. Dispersion of #2 Fuel Oil with Products A, B, C, D and E at 10:1 Oil-to-Dispersant Ratio

This sequence was determined on the basis of stabilized oil concentration levels in the liquid phase. Product B indicates that initial dispersion is efficient but, because stable emulsions are not formed, coalescence occurs readily. Migration of coalesced droplets to the surface reduces the concentration of oil in the liquid phase. On the other hand, product D forms fairly stable emulsions. The rates of dispersion for products C and E are lower than for product A.

The effect of varying the ratio of oil-to-dispersant can be seen in Figures 36 to 40. In general, higher rates of dispersion occurred as the volume of dispersant added was increased. The rate of dispersion increased significantly when the volume of Product A added was increased. Other dispersants were less effective. Products B and E did not significantly increase rates of dispersion when the oil-to-dispersant ratio was increased from 10:1 to 5:1. These results seem contrary to some manufacturers claims that oil slicks can be completely dispersed at oil-to-dispersant ratios as low as 100:1. Number 2 fuel oil is one of the easiest oils to disperse, but complete dispersion was not achieved with the dispersants tested, even when oil-to-dispersant ratio of 1:1 was used.

The concentration-time profiles displayed in Figures 41 and 42 represent the dispersion of Iranian crude and #6 fuel oil, respectively. Both oils are more difficult to disperse than #2 fuel oil. The degree of difficulty is reflected in the levels of oil concentrations that result from the dispersion of the oils with the 5 products. The concentration levels for each product are least when #6 fuel oil is dispersed. The behavior of the products in these tests was similar to their behavior in the dispersion of #2 fuel oil. Oil concentration decreased with sampling time. This series of tests was performed at a 5:1 oil-to-dispersant ratio and the following order indicates relative dispersion efficiency of the products:

Iranian Crude	D > B > A > C > E
#6 Fuel Oil	D > B > C > A > E

When the relative efficiencies of the products are compared, on the basis of these dispersion studies with the 3 oils, an important conclusion can be drawn: the relative efficiencies of the products do not depend on the type of oil. This conclusion is significant, also, as manufacturers tend to classify their products according to specific oils. It follows that a good dispersant will be effective in dispersing both "easy" and "tough" oils.

Product B was investigated in a further series of tests. Figure 43 shows the experimental data when #2 fuel oil and Iranian crude were dispersed in calm water. Low levels of oil

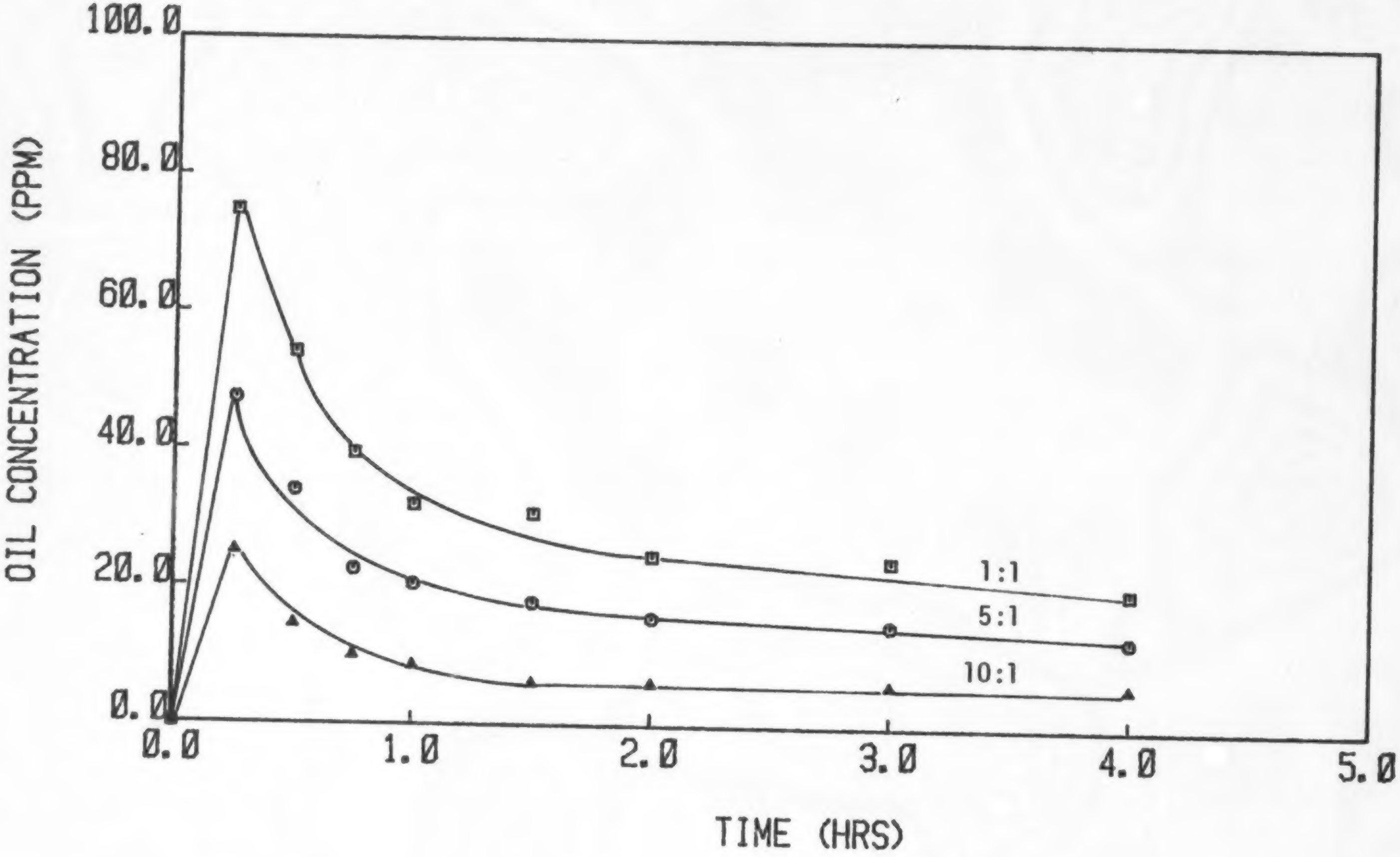

Figure 36. The Effect of Oil-to-Dispersant Ratio on the Dispersion of #2 Fuel Oil with Product A

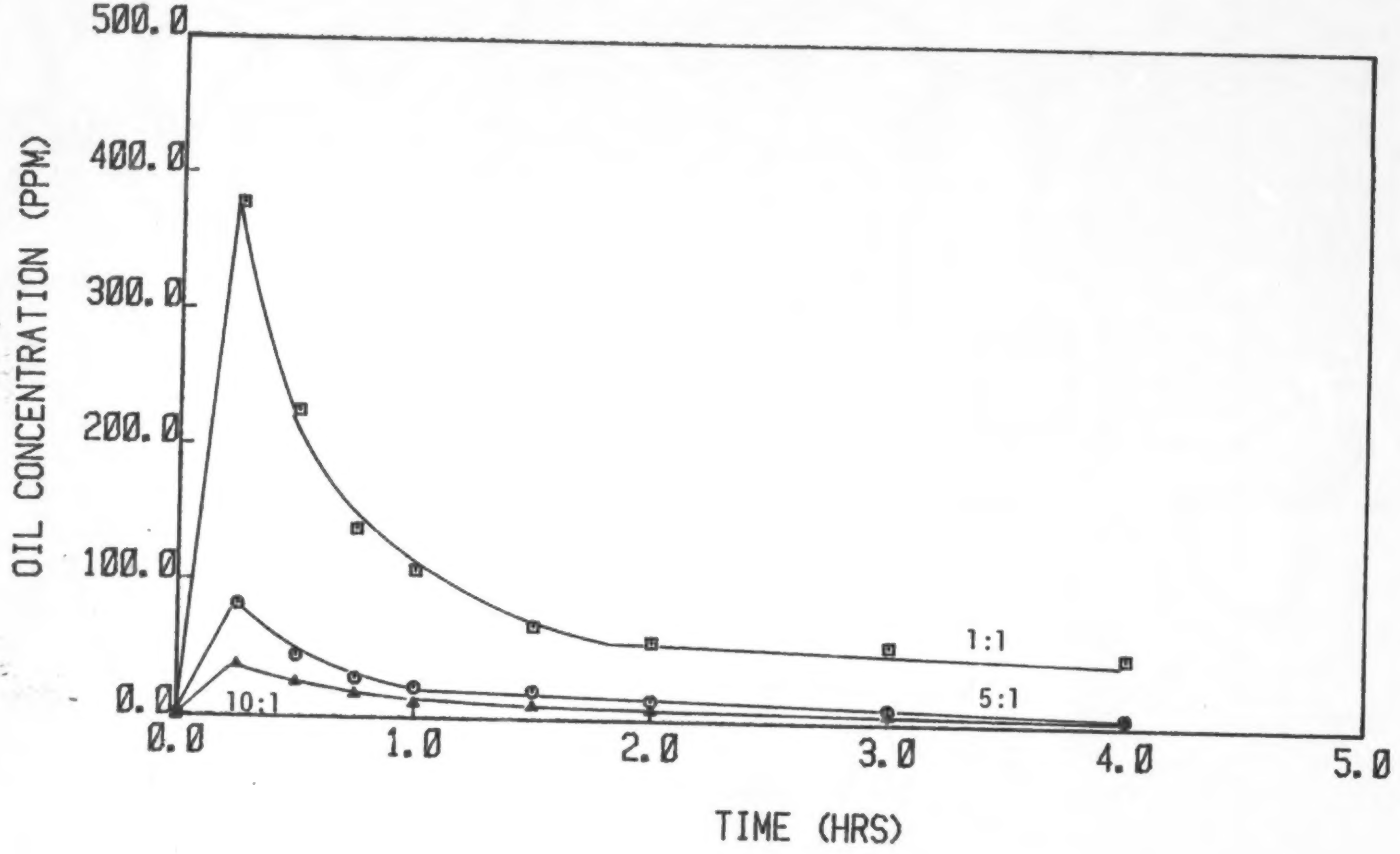

Figure 37. The Effect of Oil-to-Dispersant Ratio on the Dispersion of #2 Fuel Oil with Product B

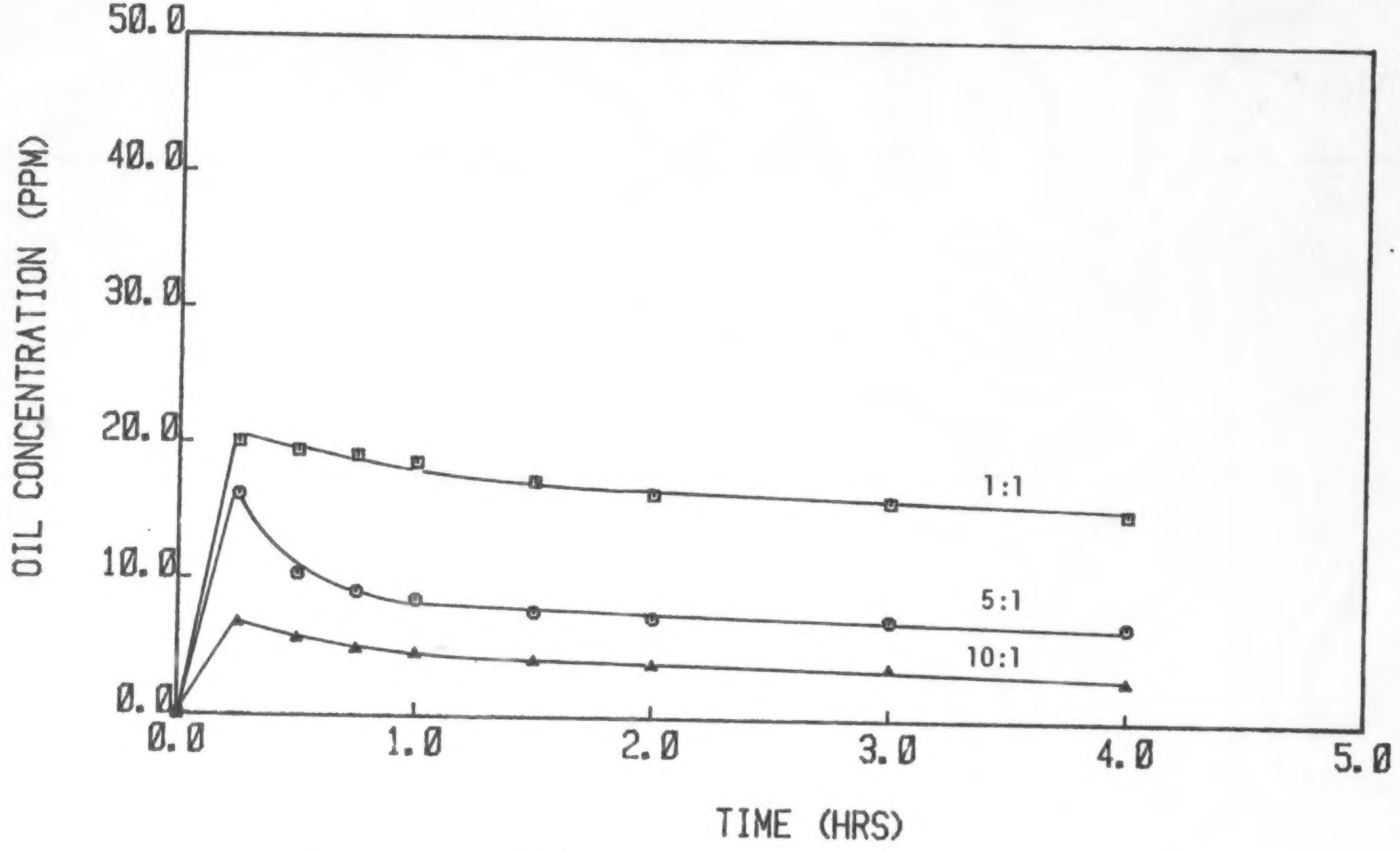

Figure 38. The Effect of Oil-to-Dispersant Ratio on the Dispersion of #2 Fuel Oil with Product C

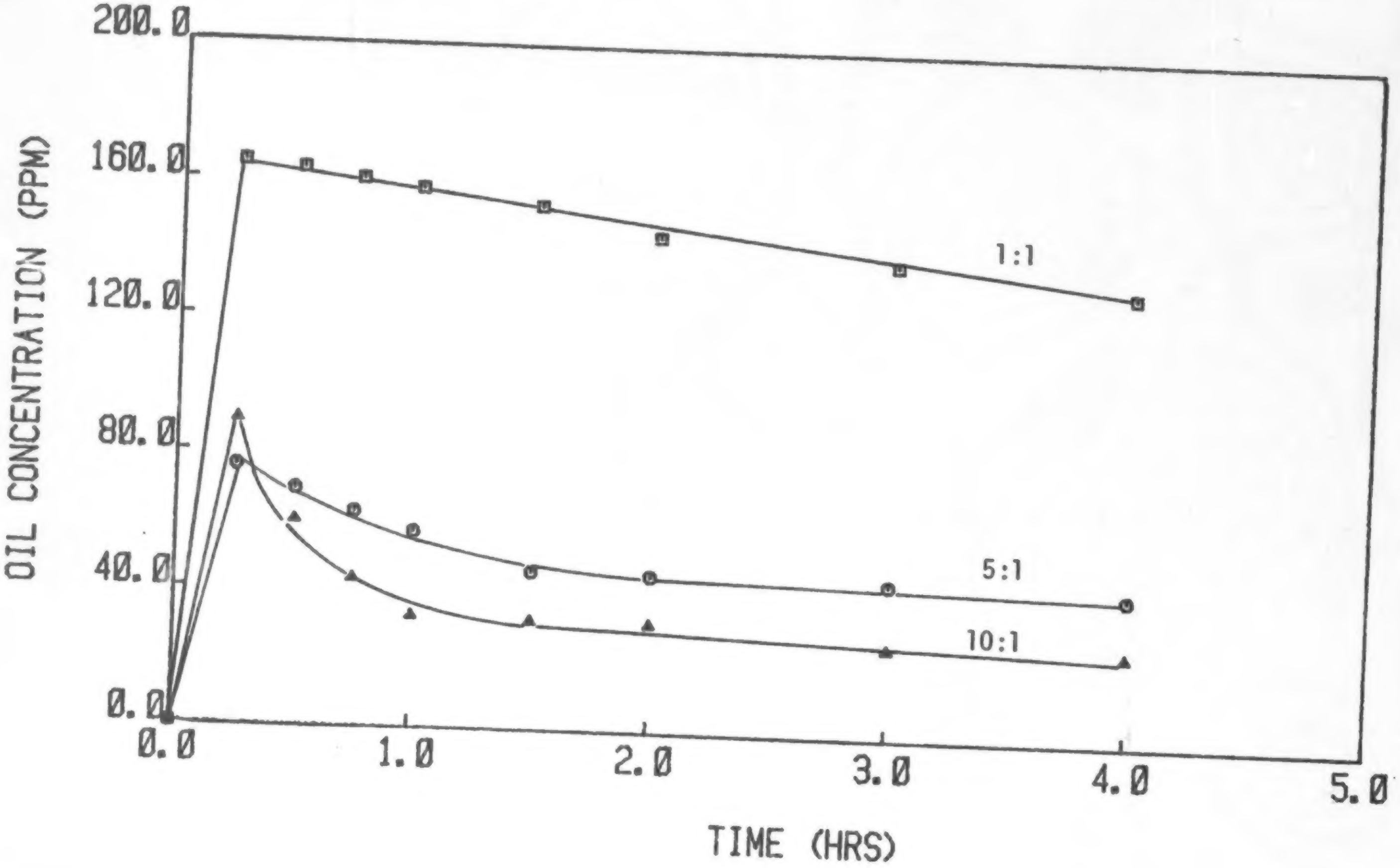

Figure 39. The Effect of Oil-to-Dispersant Ratio on the Dispersion of #2 Fuel Oil with Product D

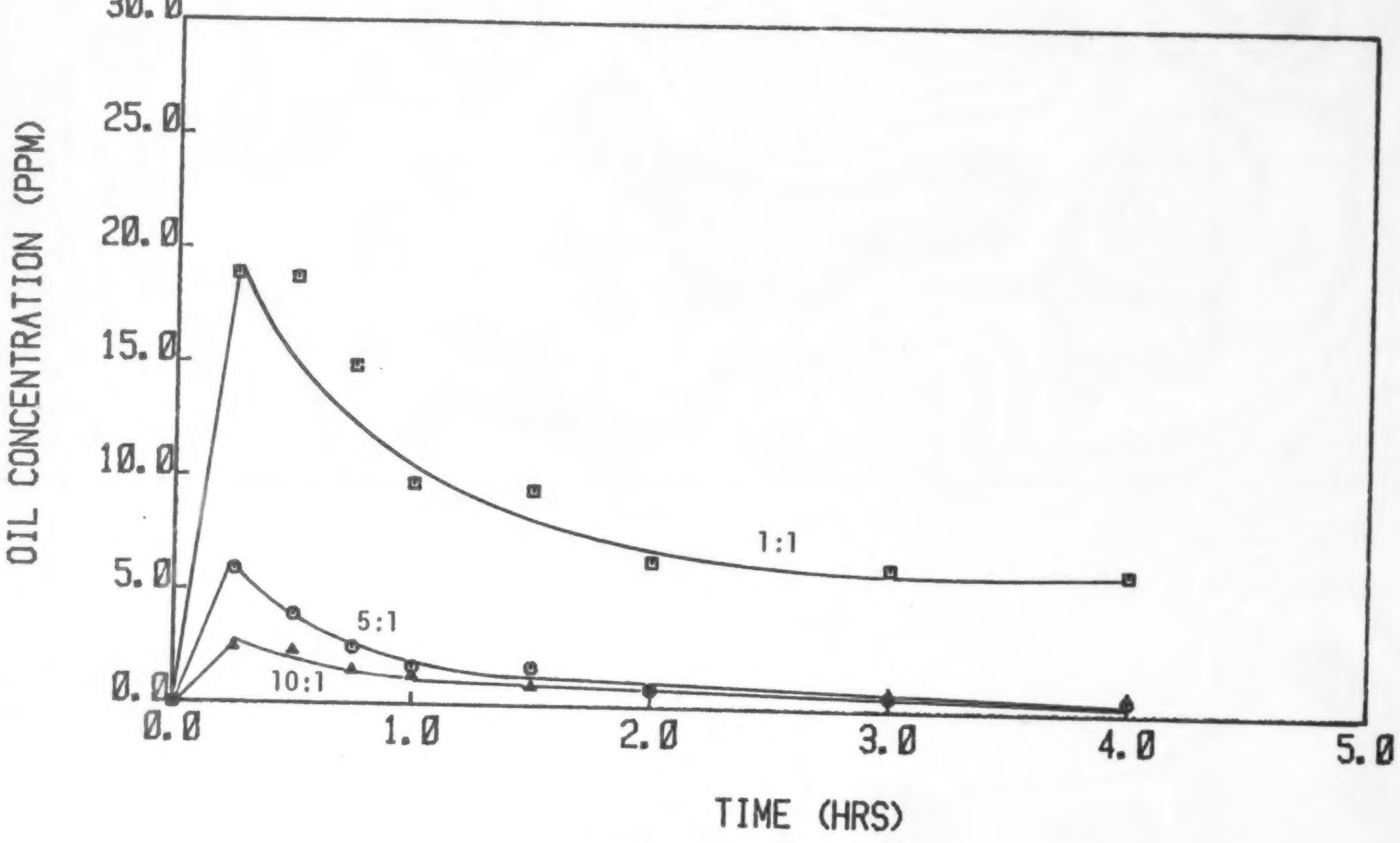

Figure 40. The Effect of Oil-to-Dispersant Ratio on the Dispersion of #2 Fuel Oil with Product E

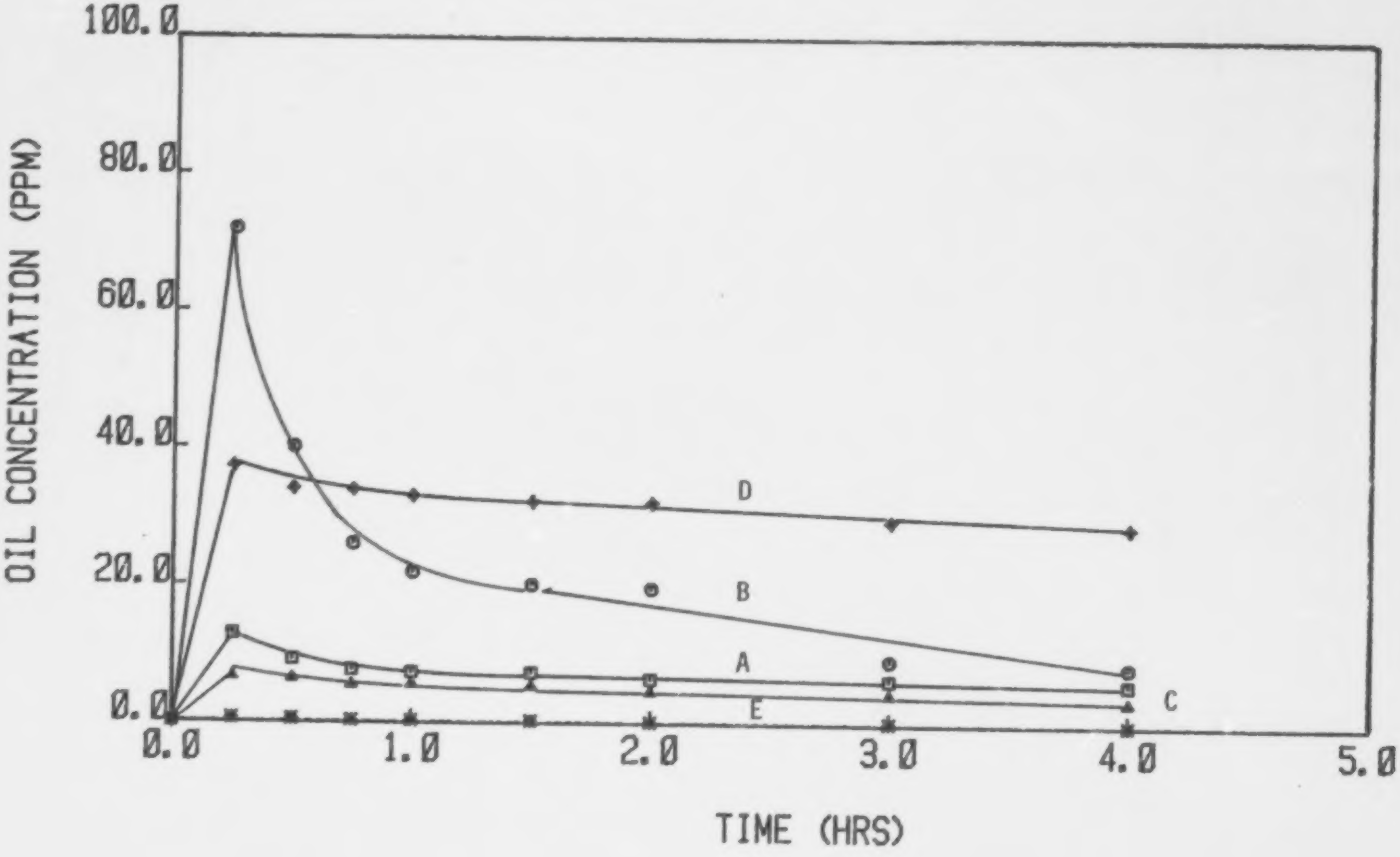

Figure 41. Dispersion of Iranian Crude with Products A, B, C, D and E at 5:1 Oil-to-Dispersant Ratio

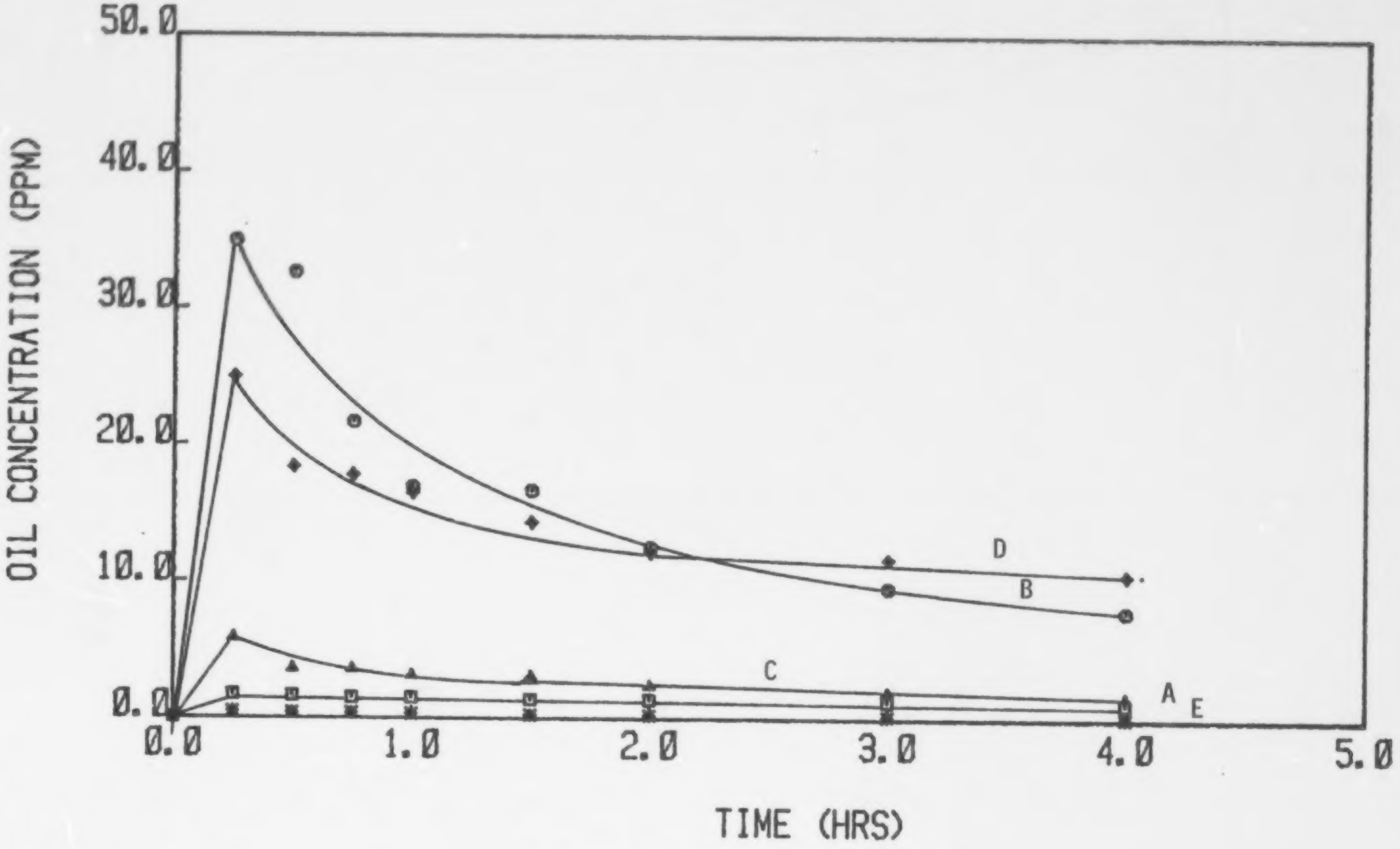

Figure 42. Dispersion of #6 Fuel Oil with Products A, B, C, D and E at 5:1 Oil-to-Dispersant Ratio

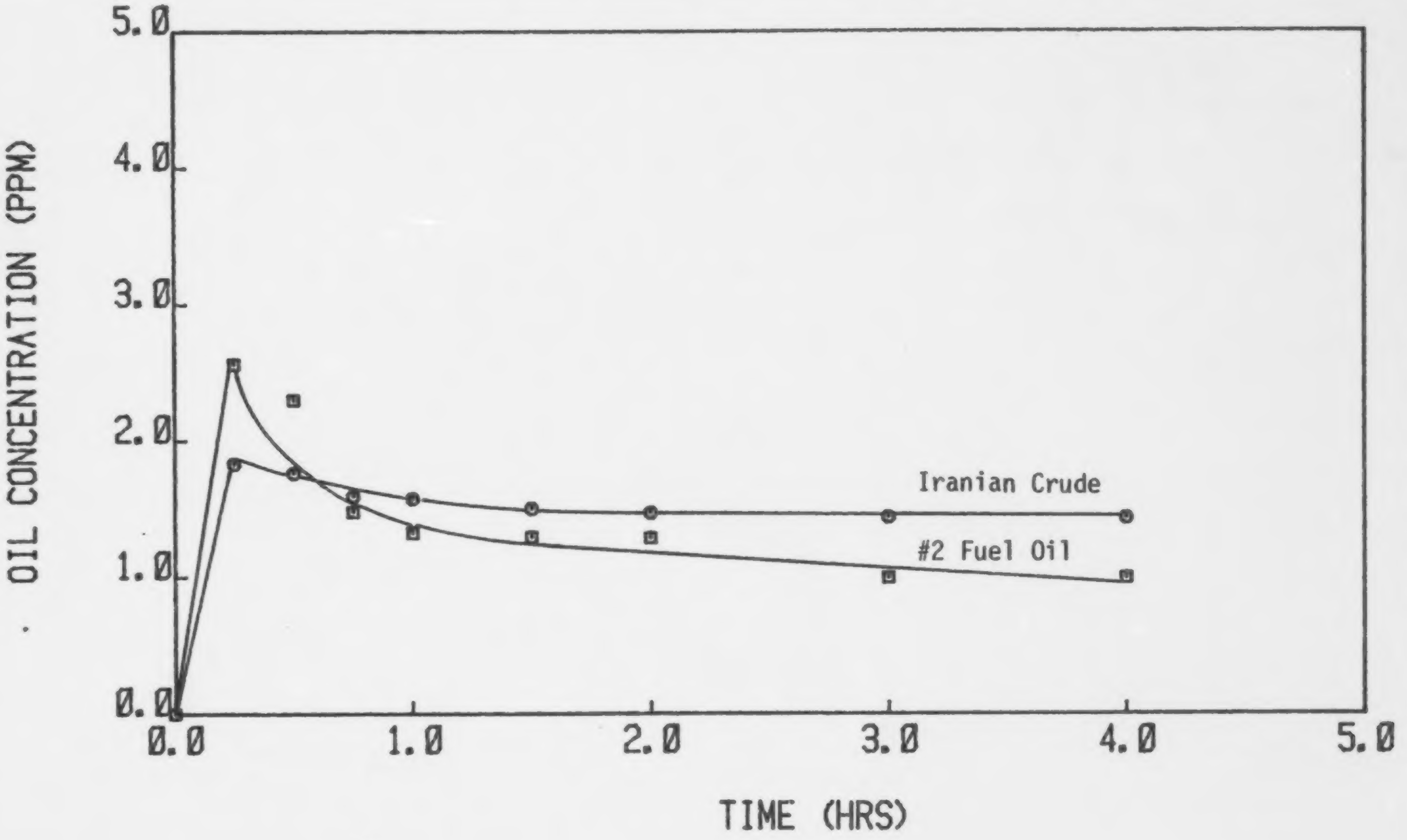

Figure 43. Dispersion of #2 Fuel Oil and Iranian Crude in Calm Water with Product B (5:1 O/D Ratio)

concentrations are achieved. In contrast, oil concentrations shown in Figure 44 are high because agitation was provided throughout the sampling period. Figures 43 and 44 suggest the importance of providing mixing to oil/water/dispersant systems, to increase rates of dispersion. Higher rates of dispersion result if the system is agitated continuously. This appears to be the ideal method to disperse oil slicks. Because of high costs associated with providing mixing energy continuously to chemically treated oils, this method of dispersion is impractical. During high sea states, mixing energy can come from gross water movements.

Finally, Figure 45 describes the dispersion of #2 fuel oil and Iranian crude in salt water. The behavior in salt water was similar to that in tap water. Except at high dilution sea salts may not have a significant effect on rates of chemical dispersion of oil slicks.

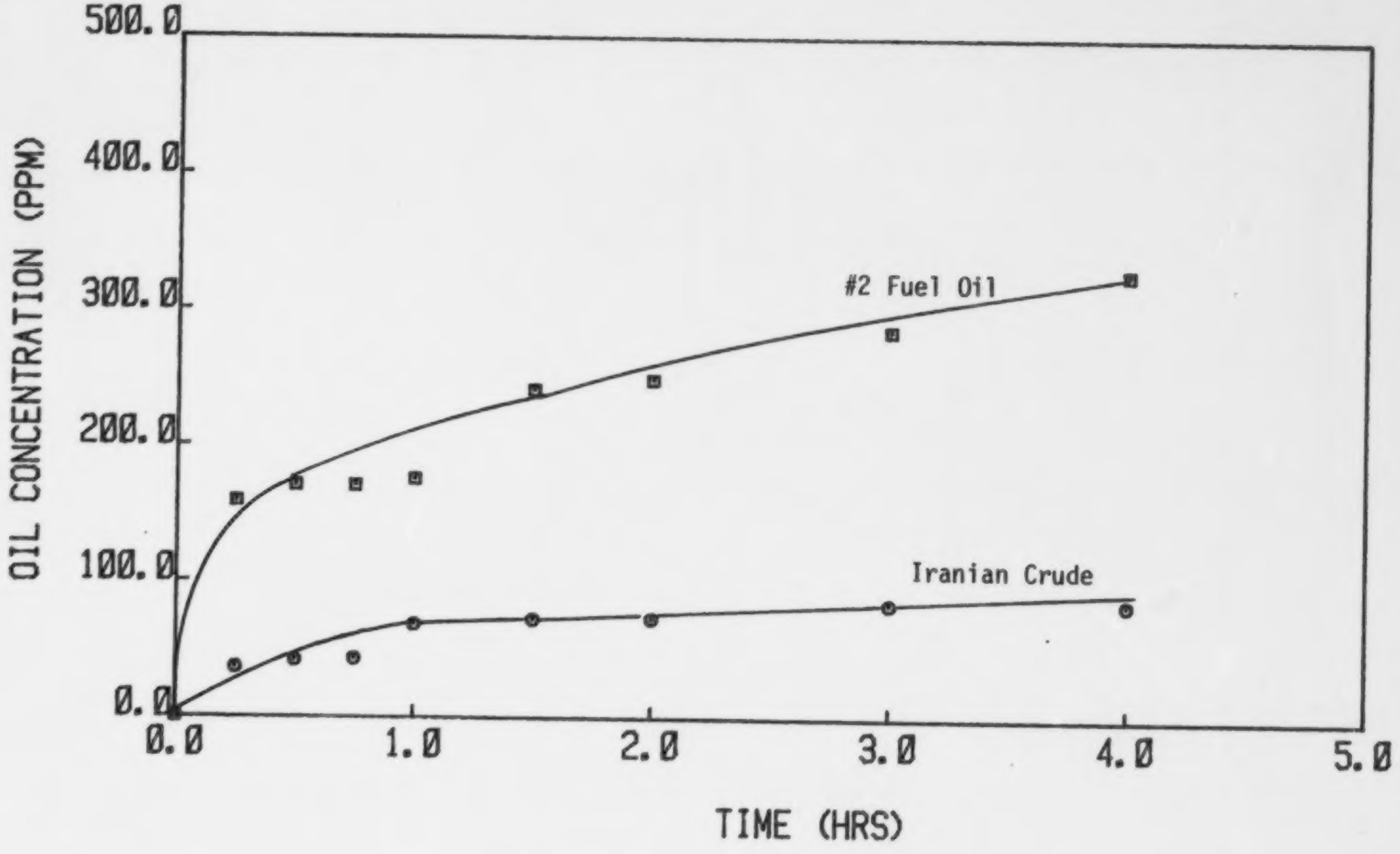

Figure 44. Dispersion of #2 Fuel Oil and Iranian Crude with Product B (5:1 O/D Ratio) Under Continuous Agitation

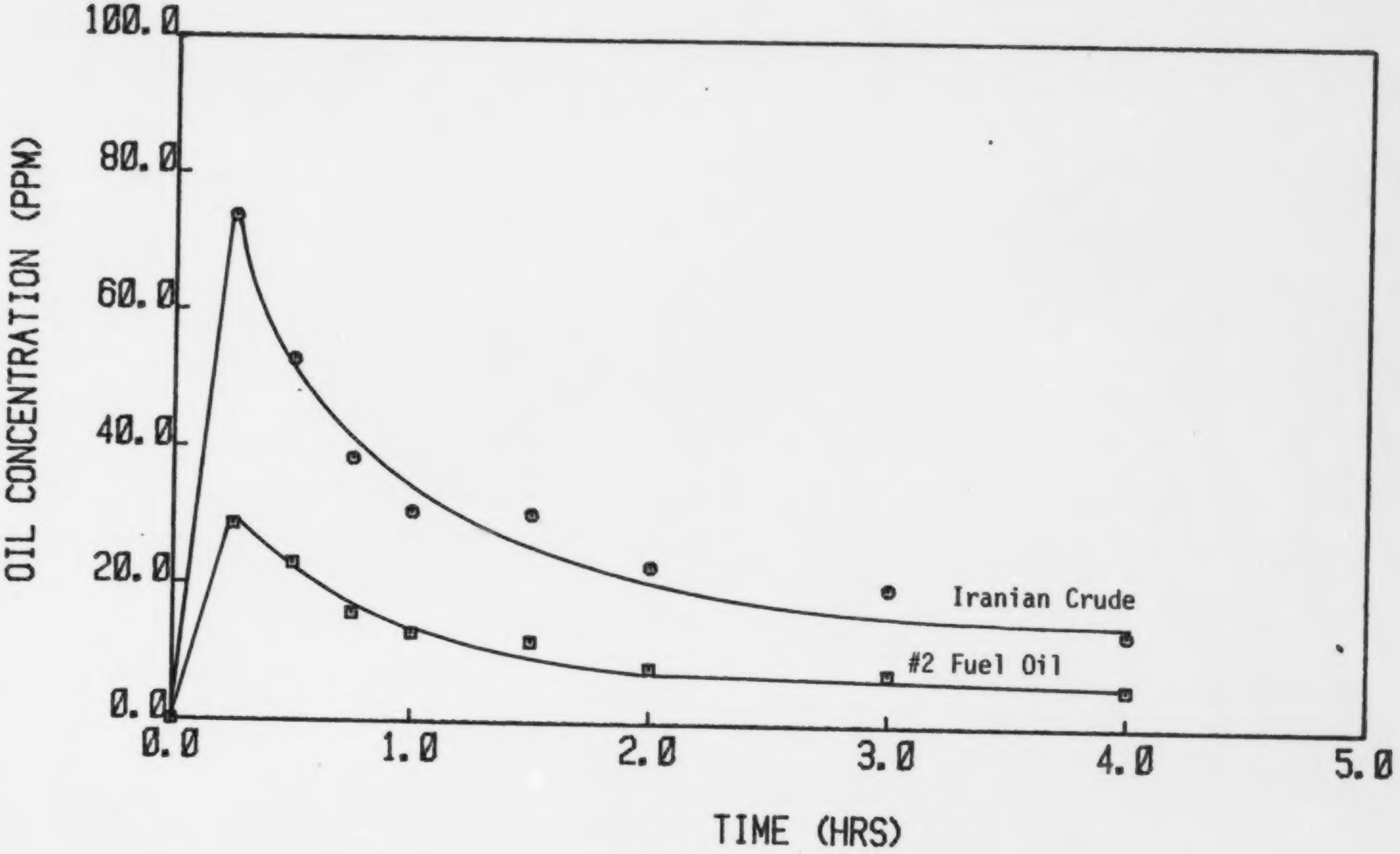

Figure 45. Dispersion of #2 Fuel Oil and Iranian Crude in Salt Water with Product B (5:1 O/D Ratio)

REFERENCES

Adamson, A. W. (1967). *Physical Chemistry of Surfaces*, 2nd edition, Interscience Publishers, New York, 747 p.

Alofs, D. J. and R. L. Reisbig (1972). An Experimental Evaluation of Oil Slick Movement Caused by Waves, J. Phys. Oceangr., 2(4), 439-443.

American Petroleum Institute (1969). *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C.

American Petroleum Institute (1971). *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C.

American Petroleum Institute (1973a). *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C.

American Petroleum Institute (1973b). *Effects of Oil and Chemically Dispersed Oil on Selected Marine Biota - A Laboratory Study*. Report by Battele, Pacific Northwest Laboratories, Washington, Publication No. 4191, API, Washington, D. C.

American Petroleum Institute (1975). *Proceedings of the Joint Conference on Prevention and Control of Oil Pollution*. API, Washington, D. C.

American Petroleum Institute (1977a). *Proceedings of the Oil Spill Conference (Prevention, Behavior, Control, Cleanup)*. API, Washington, D. C.

American Petroleum Institute (1977b). *Oil Spill Studies: Strategies and Techniques*. *Proceedings of a Workshop at Gurney's Inn, Montauk, L.I.* from Feb. 24-26, 1976, Publication No. 4286, API, Washington, D. C.

American Petroleum Institute (1977c). *Fate of Oil in a Water Environment - Phase II. A Dynamic Model of the Mass Balance for Released Oil*. Publication No. 4313, API, Washington, D. C.

American Petroleum Institute (1979). Proceedings of the Oil Spill Conference (Prevention, Behavior, Control, Cleanup). API, Washington, D. C.

Anderson, J.R.L. (1967). Guardian Survey, p. 17, April 25.

Anderson, J. W., J. M. Neff, B. A. Cox, E. H. Tatem, and G. M. Hightower (1974). Characteristics of Dispersions and Water-Soluble Extracts of Crude and Refined Oils and Their Toxicity to Estuarine Crustaceans and Fish. Mar. Biol., 27: 75-88.

Baker, J. M. (ed.) (1976). Marine Ecology and Oil Pollution, Wiley, New York.

Bancroft, W. D. (1915). J. Phys. Chem., 19, p. 363.

Berridge, S. A., R. A. Dean, R. G. Fallows, and A. Fish (1968a). The Properties of Persistent Oils at Sea. J. Inst. Pet., 54: 300-309.

Berridge, S. A., M. T. Thew, and A. G. Lorriston-Clarke (1968b). The Formation and Stability of Emulsions of Water in Crude Petroleum and Similar Stocks. J. Inst. Pet., 54: 333-357.

Blacklaw, J. R., J. A. Strand, and P. C. Walkup (1971). Assessment of Oil Spill Treating Agent Test Methods, Proceedings of Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C. 253-261 p.

Blokker, P. C. (1964). Spreading and Evaporation of Petroleum Products on Water. Presented at the 4th International Harbour Conference, June 22-27, Antwerp, Belgium.

Blumer, M. and J. Sass (1972). Oil Pollution: Persistence and Degradation of Spilled Fuel Oil. Science, 176: 1120-1122.

Boehm, P. D. and J. G. Quinn (1973). Solubilization of Hydrocarbons by Dissolved Organic Matter in Seawater. Geochim. Cosmochin. Acta, 37: 2459-2477.

Boehm, P. D. and J. G. Quinn (1974). The Solubility Behavior of No. 2 Fuel Oil in Seawater. Mar. Poll. Bull., 5(7): 101-105.

Boesch, D. F., C. H. Hershner, and J. H. Milgram (1974). Oil Spills and the Marine Environment. Ballinger Publishing Co., Cambridge, Mass.

Bohon, R. L. and W. F. Claussen (1951). The Solubility of Aromatic Hydrocarbons in Water. J. Amer. Chem. Soc., 73: 1571-1578.

Bond, W. N. (1927). Bubbles and Drops and Stokes' Law. Phil. Magazine, (7), 4, p. 889.

Boylan, D. B. and B. W. Tripp (1971). Determination of Hydrocarbons in Seawater Extracts of Crude Oil and Crude Oil Fractions. Nature, 230: 44-47.

Broecker, W. S. and T. H. Peng (1974). Gas Exchange Rates Between Air and Sea. Tellus, 26, 1-2, 21-35.

Buckmaster, J. (1973). Viscous-gravity Spreading of an Oil Slick. J. Fluid Mech., 59 (3), 481-491.

Burwood, R. and G. C. Speers (1974). Photo-oxidation as a Factor in the Environmental Dispersal of Crude Oil. Est. and Coast. Mar. Sci., 2, 117-135.

Butler, J. N. (1975). Evaporative Weathering of Petroleum Residues: The Age of Pelagic Tar. Mar. Chem., 3, 9-21.

Canevari, G. P. (1969a). The Role of Chemical Dispersants in Oil Clean-up. In: *Oil on the Sea*. (D. P. Hoult, ed.) Plenum Press, New York, pp. 29-51.

Canevari, G. P. (1969b). General Dispersant Theory. *Proceedings-Joint Conference on Prevention and Control of Oil Spills*, API, Washington, D. C., pp. 171-177.

Canevari, G. P. (1973). Development of the Next Generation Chemical Dispersant. *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C. pp. 305-308.

Canevari, G. P. (1975). A Review of the Utility of Self-Mixing Dispersants in Recent Years. *Proceedings - Conference on Prevention and Control of Oil Pollution*. API, Washington, D. C., pp. 337-342.

Canevari, G. P. (1978). Some Observations on the Mechanism and Chemistry Aspects of Chemical Dispersion, *Chemical Dispersants for the Control of Oil Spills* (L. T. McCarthy, G. P. Lindblom, and H. F. Walter, eds.), ASTM STP 659, American Society for Testing and Materials, Philadelphia, Pa. pp. 5-17.

Carberry, J. J. (1976). *Chemical and Catalytic Reaction Engineering*. McGraw-Hill Book. Co., New York, p. 642.

Chan, A. F., D. F. Evans and E. L. Cussler (1976). Explaining Solubilization Kinetics, AIChE J., 22(6), 1006-1012.

Chen, E. C., J. C. K. Overall and C. R. Phillips (1974). Spreading of Crude Oil on an Ice Surface. Can. J. Chem. Eng., 52, pp. 71-74.

Chen, E. C. and D. K. Charles (1976). Surface Tension Spreading of Crude Oil on Ice. Mar. Sci. Comm. 2, 1, 1-11.

Cochran, R. A. and P. R. Scott (1971). The Growth of Oil Slicks and Their Control by Surface Chemical Agent. J. Pet. Technol., 23, 781-787.

Cohen, Y., W. Cocchio and D. Mackay (1978). Laboratory Study of Liquid-phase Controlled Volatilization Rates in Presence of Wind Waves, Environ. Sci. Technol. 12(5), pp. 553-558.

Danckwerts, P. V. (1951). Significance of Liquid-Film Coefficients in Gas Absorption. Ind. Eng. Chem., 43(6), pp. 1460-1467.

Davies, J. T. and E. K. Rideal (1963). Interfacial Phenomena. Academic Press, New York, pp. 480.

Eganhouse, R. P. and J. A. Calder (1976). The Solubility of Medium Molecular Weight Aromatic Hydrocarbons and the Effects of Hydrocarbon Co-solutes and Salinity. Geochim. Cosmochim. Acta, 40: 555-561.

Elworthy, P. H., A. T. Florence, and C. B. Macfarlane (1968). Solubilization by Surface Active Agents. Chapman and Hall, Ltd., London, pp. 11-116.

Estes, J. E. and B. Golomb (1970). Oil Spills: Methods for Measuring their Extent on the Sea Surface. Science, 169, 676-678.

Fallah, M. H. and R. M. Stark (1976a). Movement of Spilled Oil at Sea. J. Mar. Technol. Soc., 10, 3-18.

Fallah, M. H. and R. M. Stark (1976b). Random Drift of an Idealized Oil Patch. Ocean Engng., 3: 83-97.

Fallah, M. H. and R. M. Stark (1976c). A Probabilistic Model for Dispersive Oil Losses Beneath Oil Booms. Ocean Engng., 3: 383-390.

Fannelop, T. K. and G. D. Waldman (1971). The Dynamics of Oil Slicks on Creeping Crude. Paper No. 71-14, American Inst. of Aeronautics and Astronautics, New York.

Fay, J. A. (1969). The Spread of Oil Slicks on a Calm Sea. In: Oil on the Sea (D. P. Hoult, ed.), Plenum Press, New York, pp. 53-63.

Fay, J. A. (1971). Physical Processes in the Spread of Oil on a Water Surface. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 463-467.

Fitzgerald, D. E. (1977). Utilization of Dispersants in Offshore Areas. Proceedings - 1977 Oil Spill Conference (Prevention, Behavior, Control, Cleanup). API, Washington, D. C., pp. 395-398.

Forrester, W. D. (1971). Distribution of Suspended Oil Particles Following the Grounding of the Tanker Arrow, J. Mar. Res. 29(2), 151-170.

Frankenfeld, J. W. (1973). Factors Governing the Fate of Oil at Sea: Variations in the Amounts of Dissolved or Dispersed Materials During the Weathering Process. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 485-495.

Garrett, W. D. (1969). Confinement and Control of Oil Pollution on Water with Monomolecular Surface Films. Proceedings of the Joint Conference on the Prevention and Control of Oil Spills. API, Washington, D. C., pp. 257-261.

Garrett, W. D. and W. R. Barger (1970). Factors Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water, Env. Sci. Technol., 4(2), pp. 123-127.

Giles, C. H. and S. D. Forrester (1970). Wave Damping: The Scottish Contribution, Chem. and Ind., pp. 80-87.

Glaeser, J. L. and G. P. Vance (1971). A Study of the Behavior of Oil Spills an the Arctic. U. S. Coast Guard Report No. 714108/A/001-002, NTIS, Springfield, Va.

Gordon, J. E. and R. L. Thorne (1967a). Salt Effects on the Activity Coefficients of Naphthalene in Mixed Aqueous Electrolyte Solution. I. Mixtures of Two Salts, J. Phys. Chem., 71(31), pp. 4390-4399.

Gordon, J. E. and R. L. Thorne (1976b). Salt Effects on Nonelectrolyte Activity Coefficients in Mixed Aqueous Electrolyte Solutions. II. Artificial and Natural Seawaters. Geochim. Cosmochim. Acta. 31, pp. 2433-2443.

Gordon, D. C., P. D. Keizer and N. J. Prouse (1973). Laboratory Studies of the Accommodation of Some Crude and Residual Fuel Oils in Seawater. J. Fish Res. Board Can., 30, pp. 1611-1618.

Gruenfeld, M. (1973). Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectrophotometry. Env. Sci. Technol., 7(7), pp. 636-639.

Harrison, W., M. A. Winnik, P.T.Y. Kwong, and D. Mackay (1975). Crude Oil Spills: Disappearance of Aromatic and Aliphatic Components from Small Sea-Surface Slicks. Env. Sci. Technol., 9(30), pp. 231-234.

Hartley, G. S. (1976). Micelles-Retrospect and Prospect. *Micellization, Solubilization, and Microemulsions* (K. L. Mittal, ed.) Plenum Press, New York, pp. 23-43.

Hepple, P., ed. (1971). *Water Pollution by Oil*, Inst. of Petroleum, London.

Hermann, R. B. (1972). Theory of Hydrophobic Bonding, II. The Correlation of Hydrocarbon Solubility in Water with Solvent Cavity Surface Area. J. Phys. Chem., 76(19), pp. 2754-2758.

Hess, K. W. and C. L. Kerr (1979). A Model to Forecast the Motion of Oil on the Sea, *Proceedings of the Joint Conference on Oil Spill (Prevention, Behavior, Control and Clean-up)*. API, Washington, D. C., pp. 653-663.

Hinze, J. O. (1955). Fundamentals of the Hydrodynamic Mechanism of Splitting in Dispersion Processes. AIChE J., 1, 289-295.

Hollinger, J. P. and R. A. Mennella (1973). Oil Spills: Measurements of their Distributions and Volumes by Multifrequency Microwave Radiometry. Science, 181: 54-56.

Hoult, D. P., ed. (1969). *Oil on the Sea*. Plenum Press, New York.

Hoult, D. P. (1972). Oil Spreading on the Sea. Ann. Rev. Fluid Mech., 4, pp. 341-368.

Hoult, D. P. and W. Suchon (1970). The Spread of Oil in a Channel. Fluid Mech. Lab., Dept. of Mech. Eng., Mass. Inst. Technol. 25 pp.

Hu, S. and R. C. Kintner (1955). The Fall of Single Liquid Drops Through Water. AIChE J., 1, p. 42.

Jeffrey, P. F. (1971). Large Scale Experiments on the Spreading of Oil at Sea and its Disappearance by Natural Factors. *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C., pp. 469-474.

Gruenfeld, M. (1973). Extraction of Dispersed Oils from Water for Quantitative Analysis by Infrared Spectrophotometry. Env. Sci. Technol., 7(7), pp. 636-639.

Harrison, W., M. A. Winnik, P.T.Y. Kwong, and D. Mackay (1975). Crude Oil Spills: Disappearance of Aromatic and Aliphatic Components from Small Sea-Surface Slicks. Env. Sci. Technol., 9(30), pp. 231-234.

Hartley, G. S. (1976). Micelles-Retrospect and Prospect. Micellization, Solubilization, and Microemulsions (K. L. Mittal, ed.) Plenum Press, New York, pp. 23-43.

Hepple, P., ed. (1971). Water Pollution by Oil, Inst. of Petroleum, London.

Hermann, R. B. (1972). Theory of Hydrophobic Bonding, II. The Correlation of Hydrocarbon Solubility in Water with Solvent Cavity Surface Area. J. Phys. Chem., 76(19), pp. 2754-2758.

Hess, K. W. and C. L. Kerr (1979). A Model to Forecast the Motion of Oil on the Sea, Proceedings of the Joint Conference on Oil Spill (Prevention, Behavior, Control and Cleanup). API, Washington, D. C., pp. 653-663.

Hinze, J. O. (1955). Fundamentals of the Hydrodynamic Mechanism of Splitting in Dispersion Processes. AIChE J., 1, 289-295.

Hollinger, J. P. and R. A. Mennella (1973). Oil Spills: Measurements of their Distributions and Volumes by Multifrequency Microwave Radiometry. Science, 181: 54-56.

Hoult, D. P., ed. (1969). Oil on the Sea. Plenum Press, New York.

Hoult, D. P. (1972). Oil Spreading on the Sea. Ann. Rev. Fluid Mech., 4, pp. 341-368.

Hoult, D. P. and W. Suchon (1970). The Spread of Oil in a Channel. Fluid Mech. Lab., Dept. of Mech. Eng., Mass. Inst. Technol. 25 pp.

Hu, S. and R. C. Kintner (1955). The Fall of Single Liquid Drops Through Water. AIChE J., 1, p. 42.

Jeffrey, P. F. (1971). Large Scale Experiments on the Spreading of Oil at Sea and its Disappearance by Natural Factors. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 469-474.

Klevens, H. P. (1950). Effect of Electrolytes Upon the Solubilization of Hydrocarbons and Polar Compounds. J. Amer. Chem. Soc., 72: 3780-3785.

Kolmogorov, A. N. (1949). On the Disintegration of Drops in Turbulent Flow. Doklady Akad. Nauk S.S.S.R., 66, p. 825.

Langmuir, I. (1933). Oil Lenses on Water and the Nature of Monomolecular Expanded Films. J. Chem. Phys. 1, pp. 756-776.

Leibovich, S. (1975). A Natural Limit to the Containment and Removal of Oil Spills at Sea. Ocean Engng., 3, pp. 29-36.

Leinonen, P. J., D. Mackay and C. R. Phillips (1971). A Correlation for the Solubility of Hydrocarbons in Water. Can. J. Chem. Eng., 49, pp. 288-290.

Leinonen, P. J. and D. Mackay (1973). The Multicomponent Solubility of Hydrocarbons in Water. Can. J. Chem. Eng., 51, pp. 230-233.

Lien, T. R. and C. R. Phillips (1974). Determination of Particle Size Distribution of Oil-in-Water Emulsions by Electronic Counting. Env. Sci. Technol. 8(7), pp. 558-561.

Liss, P. S. (1973). Processes of Gas Exchange Across an Air/Water Interface. Deep-Sea Res., 20, pp. 221-238.

Liss, P. S. and P. G. Slater (1974). Flux of Gases Across the Air-Sea Interface. Nature, 247: 181-184.

Lissauer, I. M. and D. L. Murphy (1979). Oil Spill Forecasting - Where is it Going. Proceedings of the Joint Conference on Oil Spill (Prevention, Behavior, Control, and Clean-up). API, Washington, D. C., pp. 649-652.

Lu, B.C.Y. and J. Polak (1973). A Study of the Solubility of Oil in Water. Technology Development Report #EPS-4-EC-76-1, EPS, Dept. of the Environment, Ontario, Canada, p. 25.

Lyons, C. G. and E. K. Rideal (1929). On the Stability of Unimolecular Films, III. Dissolution in Alkane Solutions. Proc. Royal Soc., Section A, CXXIV, p. 334.

Lysyj, I. and E. C. Russell (1974). Dissolution of Petroleum Derived Products in Water. Water Res., 8: 863-868.

Mackay, D. and P. J. Leinonen (1977). Mathematical Model of the Behaviors of Oil Spills on Water with Natural and Chemical Dispersion. Report #EPS-3-EC-77-19, EPS, Dept. of the Environment, Ontario, Canada, p. 84.

Mackay, D. and R. S. Matsugu (1973). Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water. Can. J. Chem. Eng., 51, pp. 434-439.

Mackay, D. and A. W. Wolkoff (1973). Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere. Environ. Sci. Technol., 7, pp. 611-614.

Mackay, D., J. S. Nadeau and C. Ng (1978). A Small-Scale Laboratory Effectiveness Test. Chemical Dispersants for the Control of Oil Spills (L. T. McCarthy, G. P. Lindblom, and H. F. Walter, eds.), ASTM STP 659, American Society for Testing and Materials, Philadelphia, Pa., pp. 35-49.

Marquardt, D. W. (1963). An Algorithm for Least Squares Estimation of Nonlinear Parameters. J. Soc. Ind. Appl. Math., 11(2), pp. 431-441.

McAuliffe, C. (1963). Solubility in Water of C_1-C_9 Hydrocarbons. Nature, 200 (4911): 1092-1093.

McAuliffe, C. (1966). Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cyclo-olefin, and Aromatic Hydrocarbons. J. Phys. Chem., 70(4): 1267-1275.

McAuliffe, C. (1969a). Determination of Dissolved Hydrocarbons in Sub-surface Brines. Chem. Geol., 4(1969): 478-479.

McAuliffe, C. (1969b). Solubility in Water of Normal C_9 and C_{10} Alkane Hydrocarbons, Science, 163: 478-479.

McAuliffe, C. (1977). Evaporation and Solution of C_2 and C_{10} Hydrocarbons from Crude Oils on the Sea Surface. Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems. (D. A. Wolfe, ed.). Pergamon Press, New York, pp. 33-372.

McAuliffe, C., A. E. Smalley, R. D. Groover, W. M. Welsh, W. S. Pickle and G. E. Jones (1975). The Chevron Main Pass Block 41 Oil Spill: Chemical and Biological Investigations. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 521-529.

McCarthy, Jr., L. T. (1977). Considerations for Field Use of Dispersants. Proceedings Oil Spill Conference (Prevention, Behavior, Control, Cleanup). API, Washington, D.C., pp. 399-401.

McCarthy, Jr., L. T., I. Wilder and J. S. Dorrler (1973). Standard Dispersant Effectiveness and Toxicity Tests. Environmental Protection Technology Series Report #EPA-R2-73-201, pp. 57.

McCarthy, Jr. L. T., G. P. Lindblom and H. F. Walter (1978). Chemical Dispersants for the Control of Oil Spills. ASTM Special Technical Publication No. 659, American Society for Testing and Materials, Philadelphia, Pa., p. 318.

McDevit, W. F. and F. A. Long (1952). The Activity Coefficient of Benzene in Aqueous Salt Solutions. J. Amer. Chem. Soc., 74: 1773-1777.

McMinn, T. J. (1972). Crude Oil Behavior on Arctic Winter Ice. U. S. Coast Guard Report No. 73418, NTIS, Springfield, Va.

Milz, E. A. and J. P. Fraser (1972). A Surface-Active Chemical System for Controlling and Recovering Spilled Oil from the Ocean. J. Pet. Technol., 24, pp. 255-262.

Moore, S. F. and R. L. Dwyer (1974). Effects of Oil on Marine Organisms: A Critical Assessment of Published Data. Water Res. 8, pp. 819-827.

Murphy, T. A. and L. T. McCarthy Jr. (1969). Evaluation of the Effectiveness of Oil Dispersing Chemicals, Proceedings of the Joint Conference on Prevention and Control of Oil Spills, API, Washington, D. C., pp. 199-207.

Murray, S. P. (1972). Turbulent Diffusion of Oil in the Ocean. Limnol. Oceanogr., 17(5): 651-660.

Murray, S. P. (1975). Wind and Current Effects on Large-Scale Oil Slicks. Proceedings of the Offshore Technology Conference, Dallas, Texas, Paper #OTC 2389, pp. 523-533.

National Academy of Sciences (1973a). Background Papers for a Workshop on Inputs, Fates, and Effects of Petroleum in the Marine Environment, Vol. 1, Report prepared for the Ocean Affairs Board, Office of Naval Research, Washington, D. C.

National Academy of Sciences (1973b). Background Papers for a Workshop on Inputs, Fates and Effects of Petroleum in the Marine Environment, Vol. 11, Report prepared for the Ocean Affairs Board, Office of Naval Research, Washington, D. C.

National Academy of Sciences (1975). Petroleum in the Marine Environment. Workshop on Inputs, Fates, and the Effects of Petroleum in the Marine Environment. NAS, Washington, D. C., p. 107.

Neely, W. B., G. E. Blau and T. Alfrey, Jr. (1976). Mathematical Models Predict Concentration - Time Profiles Resulting from Chemical Spill in a River. Env. Sci. Technol., 10(1): 72-76.

Nelson-Smith, A. (1972). *Oil Pollution and Marine Ecology*. Elek Science, London.

O'Brien, J. A. (1970). Oil Spreading on Water from a Stationary Leaking Source. The Chem. Engr., CE, pp. 407-409.

Oda, A. (1969). Laboratory Evaluation of Chemical Oil Dispersants, *Proceedings - Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C., pp. 199-207.

Osamor, C. A. and R. C. Ahlert (1981). A Laboratory System for Evaluating the Effectiveness of Dispersants and Criteria for Ranking Chemical Dispersants. Submitted to Environ. Sci. Technol.

Parker, C. A., M. Freegarde and C. G. Hatchard (1971). The Effect of Some Chemical and Biological Factors on the Degradation of Crude Oil at Sea. In: *Water Pollution by Oil* (P. Hepple, ed.) Inst. of Petroleum, London, pp. 237-244.

Peake, E. and G. W. Hodgson (1966). Alkanes in Aqueous Systems. I. Exploratory Investigations on the Accommodation of C_{20}-C_{33} n-alkanes in Distilled Water and Occurrence in Natural Water Systems. J. Amer. Oil Chem. Soc., 43(4): 215-222.

Peake, E. and G. W. Hodgson (1967). Alkanes in Aqueous Systems. II. The Accommodation of C_{12}-C_{36} n-Alkanes in Distilled Water. J. Amer. Oil Chem. Soc., 44(12): 696-712.

Pilpel, N. (1968). The Natural Fate of Oil in the Sea. Endeavour, 100(27): 11-13.

Poliakoff, M. Z. (1969). *Oil Dispersing Chemicals: A Study of the Composition, Properties and Use of Chemicals for Dispersing Oil Spills*. Prepared for FWPCA on Contract No. 14-12-549. U. S. Dept. of Interior, Washington, D. C., p. 27.

Pomerantz, P., W. C. Clinton and W. A. Zisman (1967). J. Colloid Interface Sci., 24: 16-28.

Prudich, M. E. and J. D. Henry, Jr. (1978). The Mechanisms of Transfer of Hydrophobic Coated Mineral Matter Particles from a Hydrocarbon to an Aqueous Phase, AIChE J., 24(5): 788-795.

Reisbig, R. L. and J. M. Pottinger (1973). The Simulation of Deep Water Waves for Oil Drift Studies. Proceedings of the Missouri Academy of Science.

Renzoni, A. (1973). Influence of Crude Oil, Derivatives and Dispersants on Larvae. Mar. Poll. Bull., 4, pp. 9-13.

Ross, C. W., P. B. Hildebrand and A. A. Allen (1978). Logistic Requirements for Aerial Application of Oil Spill Dispersants. Chemical Dispersants for the Control of Oil Spills, ASTM STP 659, (L. T. McCarthy, Jr., G. P. Lindblom and H. F. Walter, eds.) American Society for Testing and Materials, Philadelphia, Pa., pp. 66-80.

Rossini, F. D. (1960). Hydrocarbons in Petroleum, J. Chem. Educ. 37(11): 554-561.

SAS Institute (1979). A User's Guide to SAS Programming, SAS Institute, Raleigh, N. C.

Schwartzberg, H. G. (1971). The Movement of Oil Spills. Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 489-494.

Seifert, W. K. (1969). Effect of Phenols on the Interfacial Activity of Crude Oil (California) Carboxylic Acids and the Identification of Carbazoles and Indoles, Anal. Chem., 41, pp. 562-568.

Seifer, W. K. and W. G. Howells (1969). Interfacially Active Acids in a California Crude Oil. Isolation of Carboxylic Acids and Phenols, Anal. Chem., 41, pp. 554-562.

Shackleton, L.R B., E. Douglas and T. Walsh (1960). Pollution of the Sea by Oil, Trans. Inst. Mar. Engrs. (U.K.), 72(11), pp. 409-439.

Shaw, D. G. (1977). Hydrocarbons in the Water Column. Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems (D. A. Wolfe, ed.), Pergamon Press, New York, pp. 8-18.

Shaw, D. J. (1970). Introduction to Colloid and Surface Chemistry, 2nd Edition, Butterworths, London.

Shukla, D. K. and R. M. Stark (1974). Random Movement of Oil Patches. Sci. of the Total Environ., 3, pp. 117-125.

Sieburth, J. M., et al. (1976). Dissolved Organic Matter and Heterotrophic Microneuston in the Surface Microlayers of the North Atlantic. Science, 194, pp. 1415-1418.

Smith, C. L. (1977). Determination of the Leeway of Oil Slicks. In: Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems (D. A. Wolfe, ed.), Pergamon Press, New York, pp. 351-362.

Smith, C. L. and W. G. MacIntyre (1971). Initial Aging of Fuel Oil Films on Seawater. In: Proceedings of the Joint Conference on Prevention and Control of Oil Spills. API, Washington, D. C., pp. 457-461.

Smith, G. F. (1978). Techniques for Mixing Dispersants with Spilled Oil, Environmental Protection Technology Series, Report #ERA-600/2-78/128, NTIS, Springfield, Va., p. 38.

Smith, G. F. and W. E. McCracken (1977). Techniques for Mixing Dispersant Treated Oil Slicks into the Water. In: Proceedings of Oil Spill Conference (Prevention, Behavior, Control, Cleanup). API, Washington, D. C., pp. 403-406.

Smith, J. E. (1968). Torrey Canyon, Pollution and Marine Life, Cambridge University Press, Cambridge, England, p. 196.

Stolzenbach, K. D., O. S. Madsen, E. E. Adams, A. M. Pollack and C. K. Cooper (1977). A Review and Evaluation of Basic Techniques for Predicting the Behavior of Surface Oil Slicks. Report #222. School of Engineering, Massachusetts Institute of Technology, Cambridge, Mass., p. 321.

Straughan, D. (1972). Factors Causing Environmental Changes after an Oil Spill. J. Pet. Technol., 24, pp. 250-254.

Sutton, C. and J. A. Calder (1974). Solubility of Higher Molecular Weight n-Paraffins in Distilled Water and Seawater. Env. Sci. Technol., 8(7), pp. 654-657.

Sutton, C. and J. A. Calder (1975). Solubility of Alkyl Benzenes in Distilled Water and Seawater at 25°C. J. Chem. Eng. Data, 20(3), pp. 320-322.

Tanford, C. (1973). The Hydrophobic Effect, Wiley, New York, p. 200.

Tayfun, M. A. and H. Wang (1973). Monte Carlo Simulation of Oil Slick Movements. ASCE J., Waterways, Harbors and Coastal Eng. Div., 99, pp. 309-324.

Teeson, D., F. M. White and H. Schenck, Jr. (1970). Studies of the Simulation of Drifting Oil by Polyethylene Sheets. Ocean Engng., 2, pp. 1-11.

Thibodeaux, L. J. (1977). Mechanisms and Idealized Dissolution Models for High Density ($\rho > 1$), Immiscible Chemicals Spilled in Flowing Aqueous Environments. AIChE J., 23 (4): 544-553.

Ward, A.F.H. and L. Tordai (1946). Time-Dependence of Boundary Tensions of Solutions. 1. The Role of Diffusion in Time-Effects. J. Chem. Phys., 14(7), pp. 453-461.

Warner, J. L., J. W. Graham and R. G. Dean (1972). Prediction of the Movement of an Oil Spill on the Surface of Water, Paper No. OTC-155, Offshore Technol. Conf., Dallas, Texas.

Weiskopf, F. B. and M. S. Uzuner (1977). Oil Slick Spreading Beneath a Uniform Ice Cover in Presence of a Current *Proceedings of the Joint Conference on Oil Spills (Prevention, Behavior, Control and Clean-up)*. API, Washington, D. C., pp. 297-300.

Witner, F. E. and A. Gollan (1973). Determination of Crude Oil Concentration and Size Distribution in Ship Ballast Water, Env. Sci. Technol,, 7, pp. 945-948.

Wolfe, D. A., ed. (1977). *Fates and Effects of Petroleum in Marine Organisms and Ecosystems*, Pergamon Press, New York.

Wu, J. (1968). Laboratory Studies of Wind-Wave Interactions, J. Fluid Mech., 34, pp. 91-112.

Zobell, C. E. (1969). Microbial Modification of Crude Oil in the Sea. *Proceedings of the Joint Conference on Prevention and Control of Oil Spills*. API, Washington, D. C., pp. 317-326.

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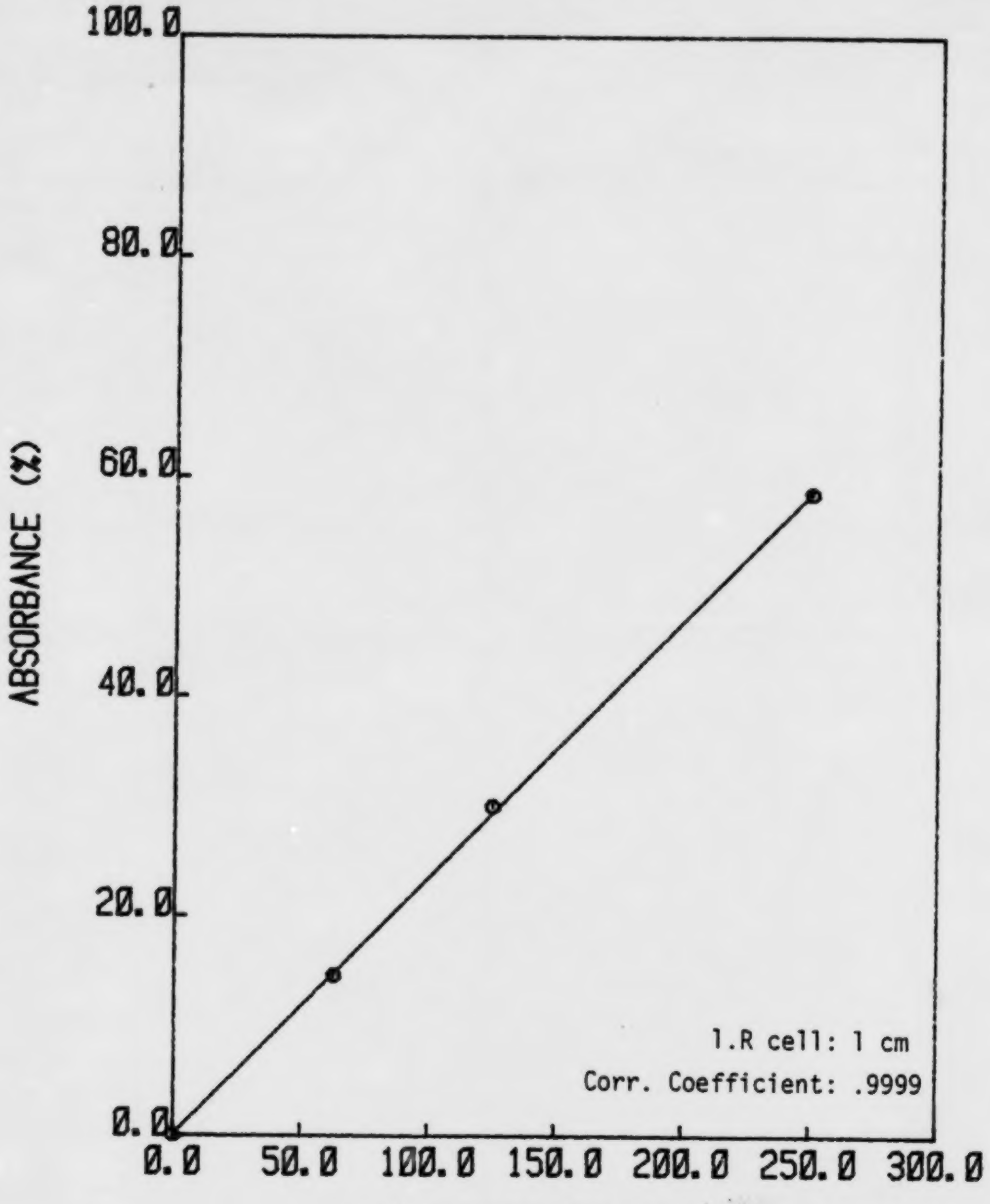

Figure A1. Calibration Curve for Nigerian Crude using 1 cm cuvets.

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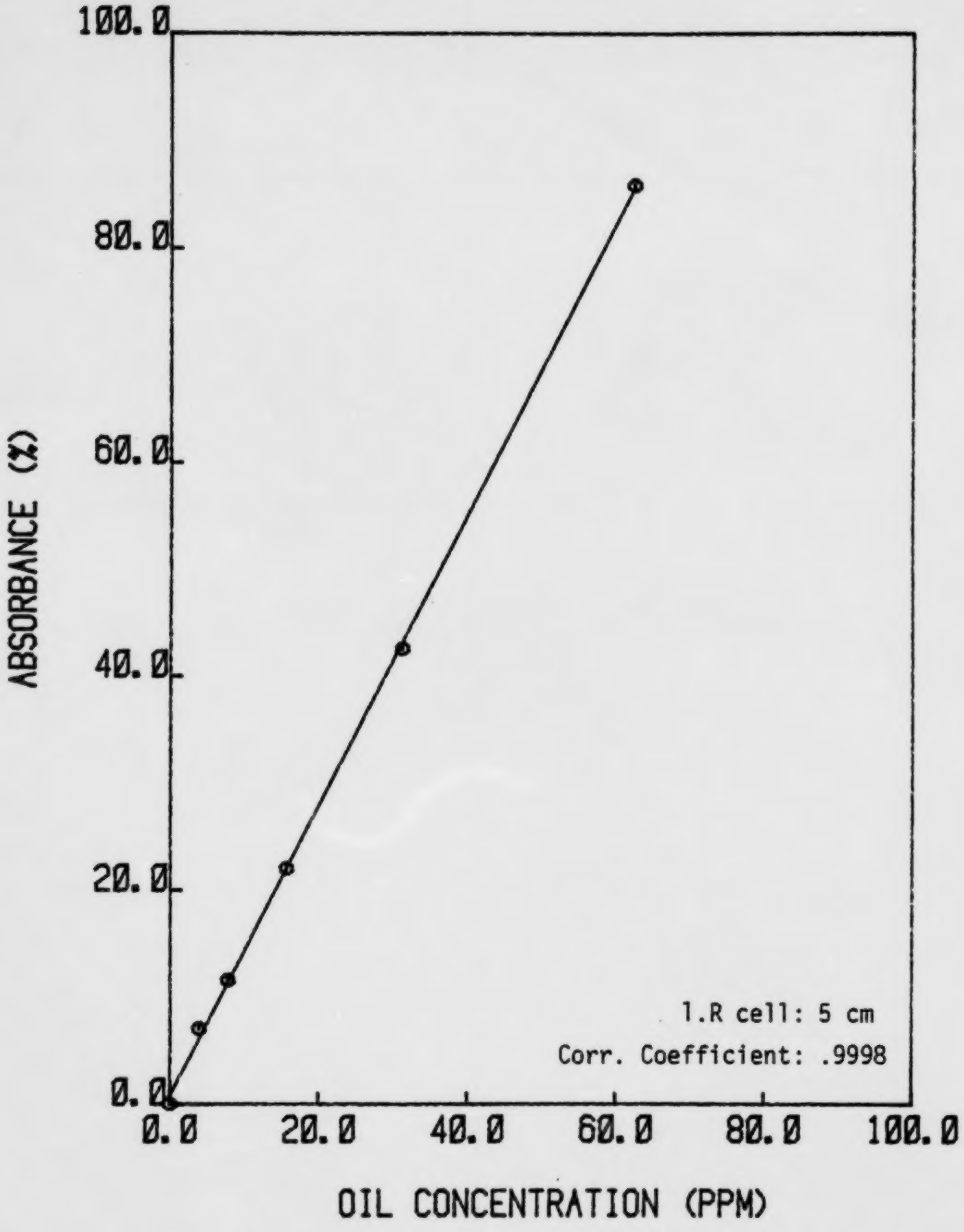

Figure A2. Calibration Curve for Nigerian Crude using 5 cm cuvets.

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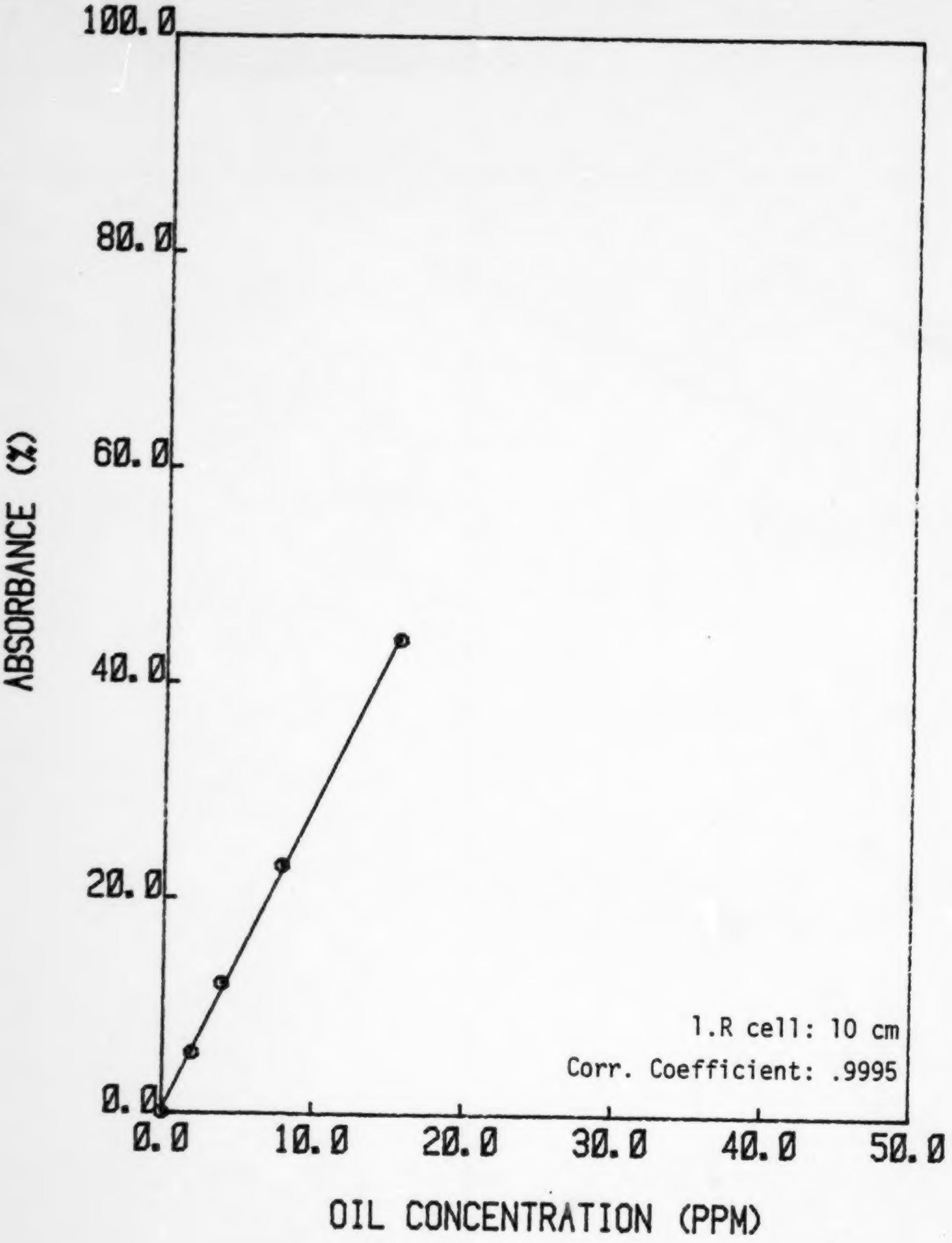

Figure A3. Calibration Curve for Nigerian Crude using 10 cm cuvets.

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APPENDIX B

SOLUBILITY DATA IN TAP WATER AT 25C

Time (Days)	Oil Concentration (PPM)					
	Nigerian	Iranian	#2 Fuel	#6 Fuel	La Rosa	Sahara
0	0.0	0.0	0.0	0.0	0.0	0.0
1	1.5	6.0	0.7	0.3	0.8	14.0
2	3.5	9.8	0.9	0.4	1.1	24.9
3	4.3	11.6	1.0	0.5	1.5	20.7
4	4.5	15.0	1.2	0.6	2.3	13.4
5	3.5	10.0	1.3	0.9	3.4	11.9
6	3.2	6.8	1.4	0.5	2.8	10.8
7	3.0	3.5	1.7	0.4	2.3	7.0
8	2.8	2.7	1.5	0.4	2.4	3.7
9	2.4	2.7	1.3	0.4	2.1	3.1
10	2.4	2.6	1.2	0.4	2.0	2.6
11	2.4	2.5	1.0	0.4	1.9	2.2
12	2.2	2.3	1.0	0.3	1.9	0.9
13	2.1	2.3	1.0	0.3	1.6	0.9
14	1.8	2.1	0.9	0.3	1.5	0.8
15	1.6	2.1			1.2	
16	1.5	2.0				
17	-	-				
18	1.5	1.8				
19	1.3	1.7				
20	1.3	1.5				
21	1.2	1.5				

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APPENDIX B (Continued)

SOLUBILITY DATA IN TAP WATER AT 25C

Time (Days)	Oil Concentration (PPM)					
	Lagunillas	Suniland	8% Crude	Alaska	Brass	Arzew
0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.5	61.2	73.4	59.1	8.2	12.5
2	0.7	15.2	78.6	81.6	8.5	13.0
3	1.1	12.4	73.9	152.1	11.0	16.0
4	1.2	8.9	47.6	75.4	13.3	28.2
5	-	6.9	37.3	70.3	37.6	58.2
6	1.9	6.5	36.0	60.9	91.5	83.4
7	1.9	6.3	32.9	52.6	108.9	131.8
8	2.3	5.4	28.4	28.5	176.0	196.0
9	2.5	4.7	26.8	20.1	159.1	89.5
10	2.2	4.8	26.3	19.8	77.9	30.5
11	2.1	4.2	20.6	18.2	52.6	23.5
12	1.9	4.1	17.9	15.4	11.3	13.5
13	1.7	4.1	13.0	15.2	5.8	13.4
14	1.6	4.2	11.8	13.9	5.3	11.0
15	1.5			14.6		

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APPENDIX C

SOLUBILITY DATA FOR SELECTED OILS IN SALT WATER AT 25C

Time (Days)	Oil Concentration (PPM)					
	Nigerian	Iranian	#2 Fuel	La Rosa	Alaska	Brass
0	0.0	0.0	0.0	0.0	0.0	0.0
1	0.4	0.6	0.9	0.7	0.4	0.7
2	0.6	0.7	1.0	1.2	0.7	0.7
3	0.9	1.0	1.2	1.3	0.8	1.2
4	0.9	1.1	1.4	1.4	1.1	1.4
5	0.9	1.2	1.5	1.4	0.6	1.3
6	1.0	1.4	1.5	1.6	0.5	1.3
7	1.1	1.5	1.4	1.7	0.6	1.2
8	1.2	1.4	1.4	2.0	0.5	1.2
9	1.2	1.4	1.3	2.3	0.5	1.2
10	-	1.4	1.2	-	0.5	-
11	-	1.4	1.0	-	0.5	-
12	1.3	1.4	1.0	2.5	0.5	1.1
13	1.3	1.4	1.0	2.5	0.5	1.1
14	1.5	1.3	1.0	2.4	0.5	1.0

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APPENDIX D

EXPERIMENTAL DATA FOR THE SPREADING OF OIL SLICKS ON CALM WATER AT 20C

TABLE D1. AREA OF OIL SLICKS FORMED BY ARZEW CRUDE

Time (mins)	Area (ft^2)			
	25^+ 1.75^*	50^+ 2.00^*	75^+ 3.27^*	100^+ 6.08^*
0	0	0	0	0
2	3.89	4.47	4.79	4.95
3	4.39	4.81	5.27	5.38
4	4.94	5.14	5.82	5.75
5	4.96	5.61	6.30	6.14
6	5.08	5.94	6.80	6.61
8	5.20	6.08	6.97	6.89
10	5.22	6.20	7.05	7.23
15	5.25	6.27	7.20	7.48
20	5.29	6.33	7.35	7.67
25	5.32	6.38	7.50	7.82
30	5.35	6.40	7.65	-
35	5.44	6.46	7.79	7.99

+ Volume of oil spilled, cm^3
* Duration of spill, min

TABLE D2. AREA OF OIL SLICKS FORMED BY BRASS RIVER CRUDE

Time (min)	Area (ft^2)			
	25⁺ 2.5*	50⁺ 4.55*	75⁺ 7.00*	100⁺ 4.53*
0	0	0	0	0
2	0.16	1.04	0.12	0.07
3	1.09	1.65	1.85	1.20
4	1.67	2.00	2.21	1.56
5	1.92	2.05	2.44	1.76
6	2.07	2.08	2.74	2.12
8	2.17	2.11	2.80	2.35
10	2.31	2.13	2.81	2.56
15	2.63	2.15	2.82	2.86
20	2.93	2.16	2.83	2.88
25	3.27	2.22	2.86	3.08
30	3.38	2.24	2.87	3.49
35	3.45	2.28	2.89	3.75

⁺ Volume of oil spilled, cm^3

* Duration of spill, min

TABLE D3. AREA OF OIL SLICKS FORMED BY ALASKA CRUDE

	Area (ft^2)			
Time (min)	25$^+$ 1.12*	50$^+$ 6.23*	75$^+$ 2.92*	100$^+$ 4.15*
0	0	0	0	0
2	4.64	4.13	3.74	4.26
3	5.22	5.20	4.18	4.76
4	5.46	6.08	4.73	5.39
5	5.63	7.11	4.92	6.10
6	5.73	7.30	5.20	6.47
8	5.83	8.01	5.41	6.64
10	6.07	8.20	5.90	7.12
15	6.69	8.77	6.23	7.43
20	7.36	8.99	6.46	7.62
25	7.80	9.17	6.69	7.80
30	8.20	9.33	6.89	7.96
35	8.56	9.49	7.08	8.10

$^+$ Volume of oil spilled, cm^3
* Duration of spill, min

TABLE D4. AREA OF OIL SLICKS FORMED BY IRANIAN CRUDE

Time (min)	Area (ft^2)			
	25^+ 3.00^*	50^+ 3.20^*	75^+ 3.40^*	100^+ 3.67^*
0	0	0	0	0
2	4.47	5.13	5.17	6.22
3	4.97	5.60	6.16	6.64
4	5.25	5.97	6.29	6.70
5	5.41	6.23	6.34	6.99
6	5.45	6.34	6.39	7.08
8	5.60	6.46	6.45	7.13
10	6.23	6.56	6.56	7.33
15	6.52	6.71	6.93	7.67
20	6.71	6.91	7.19	7.84
25	6.97	7.20	7.43	8.05
30	7.18	7.35	7.53	8.28
35	7.36	7.49	7.66	8.48

+ Volume of oil spilled, cm^3
* Duration of spill, min

TABLE D5. AREA OF OIL SLICKS FORMED BY SAHARA CRUDE

Time (min)	Area (ft^2)			
	25^+ 1.55^*	50^+ 4.00^*	75^+ 3.12^*	100^+ 7.52^*
0	0	0	0	0
2	8.58	9.33	6.49	9.14
3	9.03	9.87	6.70	9.43
4	9.45	9.99	7.49	10.21
5	9.94	10.11	7.61	10.48
6	10.32	10.19	7.98	10.66
8	10.56	10.36	8.22	11.12
10	10.77	10.58	8.37	11.15
15	10.84	10.80	8.77	11.20
20	10.86	10.92	8.94	11.29
25	10.90	10.97	9.12	11.35
30	10.97	11.01	9.28	11.46
35	11.06	11.03	9.45	11.54

+ Volume of oil spilled, cm^3
* Duration of spill, min

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TABLE D6. AREA OF OIL SLICKS FORMED BY #2 FUEL

Time (min)	Area (ft^2)			
	25$^+$ 1.83*	50$^+$ 3.70*	75$^+$ 6.73*	100$^+$ 7.22*
0	0	0	0	0
2	4.08	2.87	3.69	4.81
3	5.23	3.86	5.32	7.34
4	5.92	4.64	6.20	8.05
5	6.24	5.34	6.57	8.78
6	6.69	6.02	7.10	9.32
8	6.88	6.44	7.40	9.54
10	6.96	6.59	8.03	9.82
15	7.09	7.12	8.58	10.58
20	7.21	7.40	8.97	10.62
25	7.32	7.85	9.28	10.90
30	7.45	8.32	9.52	11.14
35	7.57	8.74	9.75	11.33

$^+$ Volume of oil spilled, cm^3
* Duration of spill, min

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TABLE D7. AREA OF OIL SLICKS FORMED BY NIGERIAN CRUDE

Time (min)	Area (ft^2)			
	25+ 1.88*	50+ 4.88*	75+ 4.63*	100+ 9.88*
0	0	0	0	0
2	0.47	1.19	0.70	0.45
3	0.73	1.64	1.18	1.05
4	1.10	1.99	1.68	1.31
5	1.53	2.16	1.80	1.64
6	1.68	2.37	2.02	1.97
8	1.83	2.57	2.44	2.26
10	2.07	2.66	2.55	2.64
15	2.48	2.77	2.80	3.34
20	2.77	2.87	3.04	4.00
25	2.99	3.11	3.19	4.57
30	3.12	3.17	3.30	5.03
35	3.23	3.19	3.39	5.40

+ Volume of oil spilled, cm^3
* Duration of spill, min

TABLE D8. AREA OF OIL SLICKS FORMED BY #6 FUEL

Time (min)	Area (ft^2)			
	25^+ 1.50^*	50^+ 1.88^*	75^+ 2.00^*	100^+ 3.23^*
0	0	0	0	0
2	0.04	0.07	0.08	0.13
3	0.10	0.14	0.09	0.22
4	0.13	0.15	0.12	0.24
5	0.15	0.17	0.14	0.27
6	0.16	0.18	0.16	0.30
8	0.17	0.20	0.19	0.32
10	0.18	0.26	0.20	0.35
15	0.19	0.32	0.27	0.40
20	0.20	0.38	0.34	0.47
25	0.22	0.43	0.43	0.57
30	0.23	0.49	0.55	0.70
35	0.26	0.55	0.72	0.88

$^+$ Volume of oil spilled, cm^3
* Duration of spill, min

TABLE D9. AREA OF OIL SLICKS FORMED BY LAGUNILLAS CRUDE

Time) (min)	Area (ft^2)			
	25^{+} 1.57^{*}	50^{+} 2.30^{*}	75^{+} 3.47^{*}	100^{+} 3.30^{+}
0	0	0	0	0
2	0.14	0.13	0.35	0.68
3	0.19	0.19	0.65	1.24
4	0.25	0.25	0.91	1.51
5	0.31	0.29	1.13	1.88
6	0.35	0.37	1.34	2.14
8	0.42	0.40	1.48	2.50
10	0.57	0.53	1.79	2.85
15	0.94	0.83	2.51	3.24
20	1.17	1.05	2.97	3.74
25	1.36	1.23	3.33	4.11
30	1.51	1.37	3.60	4.42
35	1.63	1.50	3.86	4.72

+ Volume of oil spilled, cm^3
* Duration of spill, min

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TABLE D10. AREA OF OIL SLICKS FORMED BY 8% CRUDE

Time (min)	Area (ft^2)			
	25^{+} 3.0^{*}	50^{+} 6.57^{*}	75^{+} 5.52^{*}	100^{+} 8.7^{*}
0	0	0	0	0
2	0.65	1.15	1.95	2.58
3	1.07	2.08	2.95	3.76
4	1.16	2.76	3.77	4.70
5	1.67	3.11	4.34	5.42
6	2.33	3.81	4.84	5.65
8	2.75	4.05	5.50	5.98
10	3.49	4.53	6.09	6.86
15	4.87	5.76	7.14	7.57
20	5.57	6.76	7.61	8.26
25	6.31	7.13	7.99	8.90
30	6.75	7.46	8.30	9.49
35	7.08	7.98	8.59	10.06

$^{+}$ Volume of oil spilled, cm^3
* Duration of spill, min

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TABLE D11. AREA OF OIL SLICKS FORMED BY LA ROSA CRUDE

Time (min)	Area (ft^2)			
	25^{+} 2.7^{*}	50^{+} 5.33^{*}	75^{+} 4.57^{*}	100^{+} 8.7^{*}
0	0	0	0	0
2	1.47	4.52	6.13	6.51
3	2.15	5.17	6.77	7.17
4	2.91	5.68	7.11	7.80
5	3.59	6.03	7.24	8.00
6	4.15	6.31	7.49	8.34
8	4.88	6.51	7.84	8.39
10	5.69	6.90	7.98	9.09
15	5.95	7.47	9.84	10.21
20	6.35	7.50	10.09	10.52
25	6.53	7.82	10.53	10.90
30	6.56	8.11	11.09	11.42
35	6.70	8.43	11.25	11.48

$^{+}$ Volume of oil spilled, cm^3
* Duration of spill, min

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TABLE D12. AREA OF OIL SLICKS FORMED BY SUNILAND CRUDE

Time (min)	Area (ft^2)			
	25^+ 4.07^*	50^+ 5.0^*	75^+ 5.0^*	100^+ 4.4^*
0	0	0	0	0
2	7.13	3.19	5.12	5.26
3	7.29	4.54	5.69	5.91
4	7.39	4.66	6.09	6.43
5	7.48	5.07	6.37	6.77
6	7.69	5.51	6.75	7.15
8	7.95	5.87	7.26	7.68
10	8.11	6.57	7.90	8.35
15	8.31	7.44	8.28	9.00
20	8.51	8.44	8.72	9.42
25	8.70	8.90	9.06	9.58
30	8.79	8.93	9.31	9.63
35	8.97	9.05	9.46	9.70

+ Volume of oil spilled, cm^3
* Duration of spill, min

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APPENDIX E

DATA FOR THE DISPERSION OF OILS WITH OIL DISPERSANTS

TABLE E1. DISPERSION OF #2 FUEL WITH SELECTION OIL DISPERSANTS (O/D 1:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	74.8	377.4	20.1	165.1	18.8
0.50	54.1	225.1	19.5	163.3	18.7
0.75	39.5	138.1	19.1	160.4	14.8
1.0	31.9	108.2	18.6	158.1	9.7
1.5	30.8	68.1	17.3	153.4	9.4
2.0	24.6	57.6	16.5	145.2	6.4
3.0	24.1	57.2	16.1	138.8	6.2
4.0	19.8	50.3	15.3	131.6	6.1

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TABLE E2. DISPERSION OF #2 FUEL OIL WITH SELECTED OIL DISPERSANTS (O/D 5:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	47.4	82.1	16.2	75.7	5.9
0.50	34.0	44.5	10.3	69.4	3.9
0.75	22.5	28.2	9.1	63.1	2.5
1.0	20.4	21.7	8.5	57.5	1.6
1.5	17.7	20.1	7.7	46.5	1.6
2.0	15.7	14.5	7.3	45.9	0.7
3.0	14.7	10.7	7.3	45.1	0.6
4.0	12.8	6.9	7.0	43.0	0.5

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TABLE E2. DISPERSION OF #2 FUEL OIL WITH SELECTED OIL DISPERSANTS (O/D 5:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	47.4	82.1	16.2	75.7	5.9
0.50	34.0	44.5	10.3	69.4	3.9
0.75	22.5	28.2	9.1	63.1	2.5
1.0	20.4	21.7	8.5	57.5	1.6
1.5	17.7	20.1	7.7	46.5	1.6
2.0	15.7	14.5	7.3	45.9	0.7
3.0	14.7	10.7	7.3	45.1	0.6
4.0	12.8	6.9	7.0	43.0	0.5

TABLE E3. DISPERSION OF #2 FUEL OIL WITH SELECTED DISPERSANTS (O/D 10:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	25.0	36.7	6.7	89.4	2.5
0.50	14.4	24.5	5.6	60.1	2.3
0.75	9.9	16.4	4.8	43.3	1.4
1.0	8.5	10.2	4.5	32.7	1.3
1.5	6.0	9.0	4.1	32.0	0.8
2.0	6.0	6.8	3.8	31.8	0.8
3.0	6.0	6.2	3.8	26.6	0.8
4.0	6.0	5.8	2.9	26.3	0.8

TABLE E4. DISPERSION OF IRANIAN CRUDE OIL WITH SELECTED DISPERSANTS (O/D 5:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	12.8	71.9	6.5	37.3	0.5
0.50	9.1	40.1	6.2	34.0	0.3
0.75	7.6	26.0	5.4	33.8	0.3
1.0	7.3	21.9	5.4	33.1	0.2
1.5	7.2	20.2	5.2	32.3	0.2
2.0	6.4	19.6	4.5	32.1	0.2
3.0	6.3	9.3	4.3	29.6	0.2
4.0	5.9	8.5	3.4	29.9	0.1

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TABLE E5. DISPERSION OF #6 FUEL OIL WITH SELECTED DISPERSANTS (O/D 5:1)

Sampling Time (Hours)	Concentration of Organics (PPM)				
	A	B	C	D	E
0.0	0.0	0.0	0.0	0.0	0.0
0.25	1.7	35.0	5.8	24.9	0.4
0.50	1.6	32.7	3.6	18.4	0.4
0.75	1.5	21.7	3.6	17.8	0.4
1.0	1.5	16.9	3.1	16.5	0.3
1.5	1.4	16.7	3.1	14.3	0.3
2.0	1.4	12.5	2.4	12.2	0.2
3.0	1.3	9.6	2.0	11.8	0.2
4.0	1.2	7.9	1.7	10.6	0.2

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TABLE E6. DISPERSION OF #2 FUEL AND IRANIAN CRUDE OIL WITH PRODUCT B (SALT WATER, O/D 5:1)

Sampling Time (Hours)	Concentration of Organics (PPM)	
	#2 Fuel Oil	Iranian Crude Oil
0.0	0.0	0.0
0.25	28.6	73.6
0.50	23.0	52.8
0.75	15.7	38.4
1.0	12.9	30.6
1.5	11.8	30.4
2.0	8.0	22.9
3.0	7.5	20.0
4.0	5.6	13.6

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TABLE E7. DISPERSION OF #2 FUEL AND IRANIAN CRUDE OIL WITH PRODUCT B (O/D 5:1) WITH AND WITHOUT AGITATION

Sampling Time (Hours)	Concentration of Organics (PPM)			
	#2 Fuel Oil		Iranian Crude Oil	
	Without Agitation	Continuous Agitation	Without Agitation	Continuous Agitation
0.0	0.0	0.0	0.0	0.0
0.25	2.6	158.6	1.8	36.5
0.50	2.3	170.4	1.8	41.9
0.75	1.5	170.8	1.6	43.1
1.0	1.3	175.4	1.6	69.0
1.5	1.3	241.2	1.5	72.2
2.0	1.3	248.4	1.5	73.4
3.0	1.0	285.0	1.4	84.1
4.0	1.0	327.4	1.4	84.7

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APPENDIX F

COMPUTER PROGRAMS FOR NUMERICAL ANALYSIS OF EXPERIMENTAL DATA

TABLE F1

Computer Program for Fitting Experimental Data to Dissolution Equations

```
OPTIONS LS=80;
DATA;
INPUT T C;
PROC NLIN BEST=10 METHOD=MARQUARDT;
PARAMETERS KL=.01
           KE=.04
           TM=3
           CS=29.9;
BOUNDS CS>0 TM>0;
IF T<=TM THEN DO;
MODEL C=CS*(1.0-EXP(-KL*T));
END;
ELSE DO;
MODEL C=CS*(1.0-EXP(-KL*TM))*EXP(-KE*(T-TM));
END;
OUTPUT OUT=NEW PREDICTED=CHAT;
PROC PRINT;
VAR T C CHAT;
PROC PLOT;
PLOT C*T CHAT*T='*'/OVERLAY;
*
```

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TABLE F2

Computer Program for Fitting Experimental Data to Spreading Equations

```
OPTIONS LS=80;
DATA;
INPUT T A;
INFILE T1;
PROC NLIN METHOD=MARQUARDT;
PARAMETERS K=1;
VT=25;
TD=105.0;
Q=VT/TD;
STW=73.4;
STO=28.0;
STOW=29.7;
SIGMA=STW-STO-STOW;
VISO=.01594;
IF T<TD THEN V=Q*T;
IF T>=TD THEN V=VT;
MODEL A=K*((SIGMA*V**2/VISO)**(2.0/7.0))*T**(2.0/7.0);
OUTPUT OUT=NEW PREDICTED=A1;
PROC PRINT;
VAR T A A1;
PROC PLOT;
PLOT A*T A1*T='*'/OVERLAY;
PROC NLIN METHOD=MARQUARDT;
PARAMETERS K=1;
VT=25;
TD=105.0;
Q=VT/TD;
STW=73.4;
STO=28.0;
STOW=29.7;
SIGMA=STW-STO-STOW;
SPO=.797;
IF T<TD THEN V=Q*T;
IF T>=TD THEN V=VT;
MODEL A=K*((SIGMA*T**2/SPO)**(2.0/3.0));
OUTPUT OUT=NEW PREDICTED=A2;
PROC PRINT;
VAR T A A2;
PROC PLOT;
PLOT A*T A2*T='*'/OVERLAY;
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TABLE F2 (Contd.)

```
04100    PROC NLIN METHOD=MARQUARDT;
04200    PARAMETERS K=1;
04300    VT=25;
04400    TD=105.0;
04500    Q=VT/TD;
04600    GR=980;
04700    SPO=.797;
04800    SPW=1.0;
04900    DEL=SPO/SPW;
05000    VISO=.01594;
05100    IF T<TD THEN V=Q*T;
05200    IF T>=TD THEN V=VT;
05300    MODEL A=K*((GR*SPO*(1.0-DEL)*V**4/VISO)**(2.0/11.0))*T**(2/11);
05400    OUTPUT OUT=NEW PREDICTED=A3;
05500    PROC PRINT;
05600    VAR T A A3;
05700    PROC PLOT;
05800    PLOT A*T A3*T='*'/OVERLAY;
05900    PROC NLIN METHOD=MARQUARDT;
06000    PARAMETERS K=1;
06100    VT=25;
06200    TD=105.0;
06300    Q=VT/TD;
06400    GR=980;
06500    SPO=.797;
06600    SPW=1.0;
06700    DEL=SPO/SPW;
06800    IF T<TD THEN V=Q*T;
06900    IF T>=TD THEN V=VT;
07000    MODEL A=K*((GR*(1.0-DEL)*V**2)**(2.0/7.0)*T**(4.0/7.0));
07100    OUTPUT OUT=NEW PREDICTED=A4;
07200    PROC PRINT;
07300    VAR T A A4;
07400    PROC PLOT;
07500    PLOT A*T A4*T='*'/OVERLAY;
*
```

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BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

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